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PRAESODYMIUM

[7440-10-0]

Symbol Pr; atomic number 59; atomic weight 140.908; a lanthanide-series rare earth element; belongs to the cerium group of rare earths; electron configuration [Xe] $4f^3 6s^2$; partially filled f subshell; valence states +3, +4; most stable oxidation state +3; electrode potential E°/V (aq) for $\text{Pr}^{3+} + 3e^- \leftrightarrow \text{Pr}$ is -2.35 V; atomic radius $1.828 \text{ \AA}$; first ionization potential 5.46 eV ; one naturally-occurring isotope, Pr-141; twenty-nine artificial radioactive isotopes known in the mass range 124, 126–140 and 142–154; the longest-lived isotope Pr-143, $t_{1/2}$ 13.57 day, and the shortest-lived isotope Pr-124, $t_{1/2}$ 1.2 second.

History, Occurrence, and Uses

Mosander extracted from the mineral lanthana a rare earth fraction, named didymia in 1841. In 1879, Boisbaudran separated a rare earth oxide called samaria (samarium oxide) from the didymia fraction obtained from the mineral samarskite. Soon after that in 1885, Baron Auer von Welsbach isolated two other rare earths from didymia. He named them as praseodymia (green twin) and neodymia (new twin) after their source didymia (twin). The name praseodymium finally was assigned to this new element, derived from the two Greek words, *prasios* meaning green and *didymos* meaning twin.

Praseodymium occurs in nature associated with other rare earths in a relatively high abundance. It is more abundant than some common metals such as silver, gold, or antimony. The average concentration of this metal in the earth's crust is estimated to be 8.2 mg/kg .

Praesodymium is a component of didymium glass used in welder's goggles. Its salts are used as colorants for glasses and enamels. When in glass, they produce an intense yellow color. Its oxide, praesodymium oxide, is one of the most refractory substances known and is a core material for carbon arcs used in lighting and projection. The Misch metal that contains about 5% praesodymium is used to make cigarette lighters.

Physical Properties

Pale yellow metal; attains a green oxide coating on exposure to air; exhibits two crystalline modifications; (1) an alpha form, that has a hexagonal close-packed structure, a density of 6.773 g/cm^3 and a molar volume 20.82 cc/mol , and (2) a beta form that has an open body-centered cubic structure having a density of 6.64 g/cm^3 and a molar volume of 21.20 cc/mol . The alpha form transforms to beta at 792°C .

Praesodymium metal melts at 931°C ; vaporizes at $3,510^\circ\text{C}$; paramagnetic at ambient temperatures; magnetic susceptibility at 25°C $5.32 \times 10^{-6} \text{ emu/mol}$; electrical resistivity $68.0 \times 10^{-6} \text{ ohm-cm}$ at 25°C and $132 \times 10^{-6} \text{ ohm-cm}$ at 820°C (beta-form); hardness on Vickers scale, 43 kg/mm^2 (for alpha-form); Young's modulus $3.25 \times 10^{11} \text{ dynes/cm}^2$ (based on sound velocity measurements); Poisson's ratio 0.305; thermal neutron absorption cross section 11.6 barns.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	84.99 kcal/mol
ΔG_f° (gas)	76.70 kcal/mol
S° (cry)	17.5 cal/deg mol
S° (gas)	45.4 cal/deg mol
C_p (cry)	6.50 cal/deg mol
C_p (gas)	5.11 cal/deg mol
ΔH_{fus}	1.65 kcal/mol
ΔH_{vap}	85.3 kcal/g atom
$\Delta H_{transformation}$ (alpha→beta)	0.76 kcal/mol
Coefficient of thermal expansion	$4.8 \times 10^{-6}/^\circ\text{C}$
Thermal conductivity	0.125 W/cm/K

Preparation

Praesodymium may be recovered from its minerals monazite and bastanaseite. The didymia extract of rare earth minerals is a mixture of praesodymia and neodymia, primarily oxides of praesodymium and neodymium. Several methods are known for isolation of rare earths. These are applicable to all rare earths including praesodymium. They include solvent extractions, ion-exchange, and fractional crystallization. While the first two methods form easy and rapid separation of rare earth metals, fractional crystallization is more tedious. Extractions and separations of rare earths have been discussed in detail earlier (see Neodymium and Cerium).

Praesodymium metal can be obtained from its anhydrous halides by reduction with calcium. The metal also may be prepared by electrolysis of fused praesodymium chloride at elevated temperatures (about 1,000°C). Alternatively, an eutectic mixture of praesodymium chloride, potassium chloride, and sodium chloride may be electrolyzed. In such electrolysis graphite is the anode and tungsten the cathode.

Compounds

Several compounds of praesodymium are known, mostly in +3, some in +4, and a few in other oxidation states. Its salts containing practically all anions are known. The metal reacts rapidly with dry oxygen forming praesodymium sesquioxide, Pr_2O_3 [12036–32–7], a white hexagonal solid of density 6.9 g/cm³ and melting at 2,300°C. All Pr halide salts are known: namely fluoride, PrF_3 [13709–46–1], chloride, PrCl_3 [10361–79–2], heptahydrate $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ [10025–90–8], bromide, PrBr_3 [13536–53–3], and iodide, PrI_3 [13813–23–5]. All halides are green to light green in color. The chloride, bromide and iodide salts are all hygroscopic and soluble in water and alcohol. The insoluble fluoride has a density of 6.3 g/cm³ and melts at 1,395°C. Reaction with nitric acid produces the nitrate salt which crystallizes as light green hexahydrate, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ [14483–17–1]. Praesodymium also forms binary compounds at varying nonstoichiometric compositions when heated with many nonmetals

and metalloid elements at elevated temperatures. They include the sulfide, Pr_2S_3 [12038–13–0], density 5.1 g/cm^3 and melting at $1,765^\circ\text{C}$; nitride PrN [25764–09–4] of density 7.46 g/cm^3 ; boride PrB_6 [12008–27–4], black cubic crystals of density 4.84 g/cm^3 and melting at $2,610^\circ\text{C}$; silicide PrSi_2 [12066–83–0] of density 5.46 g/cm^3 and melting at $1,712^\circ\text{C}$; and the telluride Pr_2Te_3 [12038–12–9] of density 7.09 g/cm^3 and melting at $1,500^\circ\text{C}$.

Praesodymium salts containing oxo anions such as sulfate, hydroxide, carbonate, silicates, oxalate, thiosulfate, chromate, molybdate, and borate are known.

Analysis

Praesodymium salts can be identified nondestructively by x-ray diffraction. The metal can be analyzed by atomic absorption or emission spectroscopy. The water insoluble oxide and other compounds may be digested with aqua regia, diluted, and analyzed by AA or ICP.

PROMETHIUM

[7440–12–2]

Symbol: Pm; atomic number 61; atomic weight 145; a lanthanide series inner-transition metal; electron configuration $[\text{Xe}]4f^56s^2$; partially filled f orbitals; valence states +3; ionic radius Pm^{3+} $0.98\text{\AA}$; all isotopes of promethium are radioactive; twenty-two isotopes in the mass range 134–155; longest-lived isotope Pm–145, $t_{1/2}$ 17.7 year; shortest-lived isotope Pm–140, $t_{1/2}$ 9.2 sec.

History, Occurrence, and Uses

The discovery of this element is credited to J.A. Marinsky and L.E. Glendenin who, in 1945, identified its long-lived isotope Pm–147 ($t_{1/2}$ 2.64 years) in the fission products of uranium. They named the element after Prometheus, who according to Greek mythology stole fire from heaven. The element was first isolated from fission product wastes by G.W. Parker and P.M. Lantz in 1948. It first was recovered from natural sources by O. Erametsa in 1965. An amount less than 0.5 g was recovered from 20 tons of rare earths.

Promethium does not occur in metallic form in nature. Minute quantities are associated with other rare earths. It also is detected in uranium fission products. It is probably the rarest of the lanthanide elements.

Promethium has very limited applications. It is used in phosphor lights to produce signals. Also, it is used as a beta particle source for thickness gages, nuclear batteries, and portable x-ray units.

Physical Properties

Silvery-white metal; density 7.22 g/cm^3 ; because of radioactivity, the metal and its salts luminesce in the dark giving a pale blue or greenish glow; melts

at $168\pm6^{\circ}\text{C}$; vaporizes at $2,460^{\circ}\text{C}$; insoluble in water.

Production

Promethium-147, the isotope used commercially, is isolated from fission product wastes. The radioactive materials must be handled safely in a glove box. The metal complexes either with ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) and is isolated by elution from Dowex 50.

The metal may be obtained from its fluoride salt, promethium(III) fluoride by heating with lithium metal in a double tantalum crucible at 700 to 800°C in vacuum and then increasing the temperature to $1,100^{\circ}\text{C}$.

Compounds

Promethium forms all its compounds in +3 oxidation state. Several compounds have been prepared and are well characterized. A few typical examples are pink hexagonal fluoride, PmF_3 , density 6.72 g/cm^3 ; lavender hexagonal chloride, PmCl_3 , density 4.19 g/cm^3 and yellow hydrated chloride $\text{PmCl}_3 \cdot x\text{H}_2\text{O}$; the orthorhombic coral-red bromide salt, PmBr_3 , density 5.45 g/cm^3 ; the oxide salt, Pm_2O_3 exhibiting three allotropic modifications, colors ranging from pink to coral-red with crystal systems hexagonal, monoclinic, and cubic structures; a hexagonal purple-pink hydroxide, $\text{Pm}(\text{OH})_3$, density 5.1 g/cm^3 ; a garnet-red phosphate salt, PmPO_4 , with a monoclinic crystal system and density 5.62 g/cm^3 ; and a hexagonal formate salt, $\text{Pm}(\text{HCOO})_2$ that has a pale-lavender appearance (Weigel, F., Promethium, pp 576–580 in *The Encyclopedia of Chemical Elements*, ed. C.A. Hampel, 1968. New York: The Reinhold Book Corp.)

Analysis

Promethium is identified by x-ray emission spectra, spark spectrum, and other spectroscopic methods. At extremely low concentrations, the element can be measured by ICP-MS. Also promethium and its salts can be detected from their pale-blue or greenish glow in the dark due to their radioactivity. Highly sensitive beta probes can be used for monitoring radioactive Pm-147.

Hazard

All isotopes of promethium and their salts present radiation hazard from exposure to beta and gamma rays.

PROTACTINIUM

[7440-13-3]

Symbol: Pa; atomic number 91; atomic weight 231.04; an actinide series radioactive element; an inner-transition metal; electron configuration $[\text{Rn}]5f^26d^17s^2$; valence states +4 and +5; atomic radius $1.63\text{\AA}$ (for coordination number 12); twenty-two isotopes are known in the mass range 215–218,

221–238; all are radioactive; longest-lived isotope Pa–231, $t_{1/2}$ 32, 500 years.

History, Occurrence, and Uses

In 1913 Fajans and Gohring identified the first isotope of this element, a metastable isotope having a mass 234, Pa–234m, a short-lived member of uranium–238 decay series. They named it brevium. In 1918, two independent groups, namely Hahn and Meitner and Soddy, Cranston, and Fleck simultaneously identified a longer-lived isotope Pa–231, a member of the uranium–235 decay series. The isotope Pa–234 in its ground state was discovered by Hahn and Meitner in 1921. The element derived its name from the Greek word *protos*, which means ‘first.’ Protactinium 231 occurs in the ore pitchblende at about 0.1ppm abundance. Certain ores of pitchblende have a higher abundance of this isotope, about 3ppm. Pa–231 also is found naturally in uranium and radium wastes. No commercial application of protactinium isotopes is known.

Physical Properties

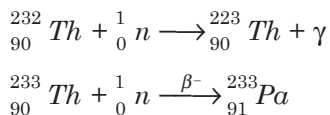
Shiny white metal with bright metallic luster; hard and malleable; body-centered tetragonal structure; density 15.37 g/cm³ (calculated); melts below 1,600°C; vapor pressure 3.88×10^{-2} torr at about 1,930°C (calculated); superconducting below 1.4°K

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	145.0 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	134.6 kcal/mol
S° (cry)	12.4 cal/deg mol
S° (gas)	47.3 cal/deg mol
C_p (gas)	5.48 cal/deg mol
Coefficient of linear expansion (0 to 700°C)	$9.9 \times 10^{-6}/^\circ\text{C}$ (calculated)

Production

Protactinium-233 is produced by the beta decay of the short-lived thorium-233. Thorium-233 is obtained by neutron capture of natural thorium-232. The nuclear reactions are as follows:



To synthesize Pa-233, thorium nitrate is irradiated with neutron. Pa-233 formed, as shown above, is dissolved in 3M nitric acid. The solution is heated. A manganous salt and permanganate are added to this solution. Manganese dioxide, MnO₂, is precipitated. Pa-233 co-deposits onto this precipitate. The precipitate is washed with water. It is then dissolved in 6M hydrochloric acid.

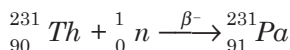
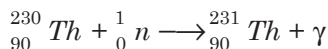
Pa-233 is extracted into diisopropyl ketone. The solvent extract containing Pa-233 is washed with 6M HCl for the removal of trace manganese salts and impurities. From the diisopropyl ketone extract, protactinium-233 is re-extracted into an HCl-HF mixture solution containing 6M HCl and 0.1M HF.

Protactinium-231 can be recovered from the residues of uranium refining by various chemical processes. One such recovery process is highlighted below (Maddock, A.G. 1968. Protactinium. In *The Encyclopedia of Chemical Elements*, ed. C.A. Hampel, pp 580-585. New York: Reinhold Book Corp).

The isotope Pa-231 is extracted with a mixture of 8M HCl and 0.1M HF from the uranium refining residues. Protactinium converts to its fluoride, PaF_4 . Addition of boric acid or aluminum converts PaF_4 into a complex, which is extracted into diisopropyl ketone. The organic solution is washed and the Pa-complex is re-extracted into HCl-HF mixture. After repeated extractions, the diisopropyl ketone solution is treated with oxalic acid to reduce any iron salts present as contaminants. The solution is then treated with potassium hydrogen fluoride, KHF_2 , to precipitate protactinium as K_2PaF_7 . The precipitate is filtered and dissolved in sulfuric acid. Treatment with hydrogen peroxide forms a precipitate of protactinium peroxide, thus separating it from niobium. Peroxide on ignition forms diprotactinium pentoxide, Pa_2O_5 .

Other reagents can be employed to recover protactinium from uranium refining residues or wastes. For example, treatment with 4M phosphoric or iodic acid precipitates protactinium as phosphate or iodate which is soluble in HF.

Protactinium-231, similar to Pa-233, also can be synthesized by neutron bombardment of thorium-230:



Compounds

The two oxidation states of protactinium are +4 and +5. In solution, Pa^{4+} is oxidized to Pa^{5+} by atmospheric oxygen. The chemistry of pentavalent protactinium is quite similar to that of niobium and tantalum. In acid medium, several metal ions at high concentrations co-precipitate protactinium. When heated with hydrogen at 300°C, protactinium forms a hydride that probably has a composition PaH_3 . A few selected compounds of protactinium include the black cubic oxide PaO_2 and the white hexagonal pentoxide Pa_2O_5 ; the tetragonal oxide sulfide PaOS of pale yellow color; the tan colored monoclinic fluoride, PaF_4 and the white tetragonal pentafluoride, PaF_5 ; the greenish-yellow tetragonal chloride, PaCl_4 ; and the pale yellow monoclinic pentachloride, PaCl_5 ; a black orthorhombic pentaiodide, PaI_5 ; and an orange red orthorhombic pentabromide, PaBr_5 . A number of other salts and complexes are known.

Analysis

Protactinium is separated by solvent extraction and anion exchange processes by using sulfate solutions. After chemical separation, the protactinium salts are ignited to a pentoxide, Pa_2O_5 , which may be converted into an arsenazo(III) complex. The absorbance of the solution is measured at 630 nm with a spectrophotometer. Protactinium-231 is an alpha emitter and also forms photons at 300 KeV, which can be measured by various radioactive counters and spectrophotometric techniques. Protactinium also can be measured by neutron activation analysis.

Toxicity

Protactinium is a very dangerous substance to work with. It is highly toxic and presents a radiation hazard (alpha emitter). The Pa-231 isotope is a long-lived alpha-emitter which is not excreted out readily. Exposure can cause cancer.

RADIUM

[7440-14-4]

Symbol Ra; atomic number 88; atomic weight 226; a Group II (Group 2) alkaline-earth element resembling chemically to barium; a radioactive element; electron configuration $[\text{Rn}]7s^2$; valence state +2; four naturally-occurring isotopes: radium-223, a member of the uranium-235 series, $t_{1/2}$ 11.6 days; radium-224, a member of the thorium series, $t_{1/2}$ 3.6 days; radium-226, a member of the uranium-238 series, $t_{1/2}$ 1,600 years; radium-228, a member of the thorium series, $t_{1/2}$ 1.9 year; while the isotopes Ra-233, -224, and -226 are alpha emitters, Ra-228 is a beta-emitter; the total number of isotopes including the above four naturally-occurring isotopes are twenty-nine, having mass numbers 206 to 234.

History, Occurrence, and Uses

Radium was discovered in 1898 by Marie Curie, collaborating with her husband Pierre Curie and G. Bemont. They recovered this element from the naturally-occurring uranium ore, pitchblende. Tons of pitchblende were extracted to obtain less than 500mg of radium. Radium repeatedly was concentrated, first into the barium fraction of their residues and then separated from barium by fractional crystallization. Marie Curie named the new element radium. This name was originally assigned to its isotope Ra-226. However, radium currently refers to all isotopes of the element having atomic number 88. She purified a radium salt to determine its atomic weight. This was done by dissolving radium sulfate in sodium carbonate solution and then converting the radium carbonate formed as its chloride by dissolving in hydrochloric acid. Repeated fractionation gave pure radium chloride, RaCl_2 , from which Mme Curie derived an atomic weight of 225.18. This value closely agreed with the atomic weight 225.97 obtained several years later by Honigschmid, using other methods.

Radium occurs in small quantities in all uranium minerals. It is a daugh-

ter element of uranium, i.e., one of its radioactive disintegration products. The mineral carnotite, found in the USA, contains about 10mg radium per ton. Radium has been detected in many groundwaters in the USA.

Radium salts have several applications. Historically, it was used in cancer treatment for destroying malignant tumors. At present, such use has been considerably reduced, replaced by readily available and low cost radioisotopes such as cobalt-60. Its gamma radiation is used for irradiating metals to detect any fractures in welding. Radium, in minute proportion, is mixed with phosphors (substances that emit light when irradiated) and used to make luminous paints and watch dials. Radium compounds are used to remove static electricity from textile products. Its gamma rays ionize the air, making the air able to remove static electricity from surfaces.

Radium-226 also is a source material to produce radon-222 in several radiotherapy treatments. Radon-222, the first daughter of radium-226, is safer to use because of its much shorter half-life of 3.8 days. Curie (Ci), the internationally adopted unit for radioactivity, is based on the emanation of alpha particles by radium-226. This unit is equal to the number of alpha particles emitted by 1g of radium in any form per second. One curie is equal to 3.70×10^{10} alphas/sec.

Recovery

Radium is an intermediate member of the uranium decay series. Therefore, it is present in all uranium minerals. Its abundance in uranium is calculated to be about 0.33ppm.

Uranium mineral first is digested with hot nitric acid. All uranium and radium compounds dissolve in the acid. The solution is filtered to separate insoluble residues. The acid extract is then treated with sulfate ions to separate radium sulfate, which is co-precipitated with the sulfates of barium, strontium, calcium, and lead. The precipitate is boiled in an aqueous solution of sodium chloride or sodium hydroxide to form water-soluble salts. The solution is filtered and the residue containing radium is washed with boiling water. This residue also contains sulfates of other alkaline earth metals. The solid sulfate mixture of radium and other alkaline earth metals is fused with sodium carbonate to convert these metals into carbonates. Treatment with hydrochloric acid converts radium and other carbonates into chlorides, all of which are water-soluble. Radium is separated from this solution as its chloride salt by fractional crystallization. Much of the barium, chemically similar to radium, is removed at this stage. Final separation is carried out by treating radium chloride with hydrobromic acid and isolating the bromide by fractional crystallization.

Radium in hydrochloric acid solution may be separated effectively by ion exchange methods using cation exchange-resin columns. A weak HCl solution is passed through the column. The absorbed metals on the ion-exchange column are eluted with ethylenediaminetetraacetic acid (EDTA) at pH 6.25 or with ammonium citrate at pH 7.8. With either eluant, radium is eluted last, after removing barium and then lanthanum, calcium, magnesium, and other metals.

Reactions

The chemistry of radium is very similar to its Group IIA alkaline-earth analog barium. The metal forms a number of salts in its +2 valence state, the only valence state typical of all alkaline earth metals. The few salts that are of commercial use include chloride, RaCl_2 , bromide RaBr_2 , and sulfate, RaSO_4 .

Analysis

Gross alpha and gross beta activity can be determined by various radioactive counters, such as internal proportional, alpha scintillation, and Geiger counters. Radium in water can be measured by co-precipitating with barium sulfate followed by counting alpha particles. Radium-226 can be measured from alpha counting of radon-222. Various methods are well documented (APHA, AWWA, and WEF•1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington DC: American Public Health Association).

Hazard

The radiation from radium can cause cancer in the lung, osteogenic sarcoma, blood dyscrasias and injury to skin. Inhalation, ingestion, skin contact or body exposure to radium and all its salts must be avoided.

RADON

[10043–16–4]

Symbol: Rn; atomic number 86; atomic weight 222; a radioactive noble gas element; heaviest of the noble gases; electron configuration $1s^2 2s^2 2p^6 3s^2 \cdot 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$; valence 0; one of the intermediates of uranium-238 series; first daughter of radium-226; eighteen isotopes are known; all radioactive; the longest-lived isotope Rn-222, $t_{1/2}$ 3.823 day.

History, Occurrence, and Uses

Three isotopes of radon were discovered around 1900. Rutherford found that thorium continuously produced a radioactive gas, which was swept away by air. He called this gaseous radioactive product “thorium emanation.” Dorn, around the same time, found that radium also evolved a gaseous radioactive daughter known as “radium emanation.” A third gas was found among products of actinium decay by Debierne in 1900. This was termed “actinium emanation.” All the three emanations were isotopes of element 86. They were thoron, radon, and actinum, respectively, corresponding to their atomic masses of 220, 222, and 219. The name radon was adopted for the entire element 86 in 1923. The spectrum of radium emanation (Rn-222) appeared similar to that of argon, krypton, and xenon. The gas is chemically inert like other noble gases. The element was assigned an atomic number 86 and placed as a noble gas below xenon in the Periodic Table.

Radon occurs in deep earth gases. Many products are emitted continuous-

ly from uranium deposits in the earth's crust. Trace concentrations of radon are found in its groundwaters, in the basements of many houses, and in household air. Radon diffuses partially from radium salts and deposits its radioactive decay products on surrounding objects.

Radon is a radiation source for treating cancer. It is safer than radium-226 because of its much shorter half-life. Its solution in petroleum jelly is used in some ointments for treating certain skin diseases. The non-medical uses of radon include its application as a gaseous tracer to detect leaks; to measure flow rates; as a source of neutron in radon-beryllium mixtures; to ionize gases to promote radon-induced chemical reactions such as oxidation, decomposition, and polymerization; to measure reaction rates, and in other kinetic studies; and as a point source of gamma rays in radiography to inspect welding and castings of metals.

Physical Properties

Colorless gas; density about 9.73 g/L at STP; liquefies at -61.8°C ; density of liquid radon 4.4g/mL at -62°C ; solidifies at -71°C to an opaque crystalline solid; density of solid radon 4.0 g/cm³; critical temperature 104.4°C ; critical pressure 62.4 atm; viscosity 2.13×10^{-4} poise at 0°C (estimated); strongly absorbed onto surfaces; dissolves in water, 230 mL/L at 20°C ; slightly soluble in alcohol and other organic solvents .

Thermochemical Properties

ΔH_f°	0.0
$\Delta H_f^{\circ} (\text{Rn}^+)$	249.3 kcal/mol
ΔG_f°	0.0
S°	42.1 cal/deg mol
C_p	4.97 cal/deg mol

Production

Radon can be isolated from radium by several methods. An aqueous solution of radium salt such as radium bromide is heated, liberating radon. Radioactive bombardment then decomposes water to oxygen and hydrogen. Radon is separated from the gaseous mixture by condensation in tiny tubes placed in liquid air. The tubes then are sealed by melting. A gold or platinum coating is applied to form the "radon seeds" used in radiation therapy.

Alternatively, a slightly acid solution of a soluble radium salt such as chloride or bromide is placed in a soft-glass vessel behind lead shielding. The solution is boiled. Radon is pumped out as needed and frozen into a cold trap at -95°C . Hydrogen and oxygen are the main impurities generated from electrolytic decomposition of water. They are recombined by sparking or applying a hot wire. Carbon dioxide, water vapor, acid vapor, and hydrocarbon impurities are removed by various chemical methods.

Radon can be obtained from radium salts in the solid phase too. At ordinary temperatures, certain mixtures containing radium salts such as radium mixed with barium, radium palmitates, or gels of radium mixed with iron(III) hydroxide or aluminum(III) hydroxide efficiently release radon. Although any

radium salt would emit radon, the latter can diffuse very slowly at room temperature through the walls of the container vessels. However, when a radium salt is heated above 600°C radon diffuses rapidly through the solid container vessels and escapes.

Radon also may be separated from gas streams by adsorption on activated charcoal or silica gel. At temperatures colder than dry ice, charcoal is an excellent adsorbent. Radon may be desorbed by heating the adsorbent in vacuum at 350°C.

Analysis

Radon-222 may be transported with a carrier gas into an ionization chamber and its alpha particles counted. Short-lived isotopes in a carrier gas stream are measured this way using a flow-type ionization chamber.

Hazard

Exposure to radon can cause lung cancer.

RHENIUM

[7440–15–5]

Symbol: Re; atomic number 75; atomic weight 186.21; a Group VIIB (Group 7) transition metal of manganese triad; electron configuration $[\text{Xe}]4f^{14}5d^56s^2$; valence states $-1, +1, +2, +3, +4, +5, +6, +7$; most common valence state, $+7$; two naturally occurring isotopes: Re-185 (37.40%), Re-187 (62.60%); Re-187 is radioactive with $t_{1/2}$ 4.5×10^{10} year; twenty-seven artificial radioisotopes in the mass range, 162–170, 172, 174–184, 186, 188–192.

History, Occurrence, and Uses

The element was discovered in 1925 by Walter Noddack, Ida Tacke Noddack, and O. Berg. They detected it by x-ray examination of platinum ores. X-ray studies also showed its occurrence in columbite and other minerals. It was named after the German river Rhine, called Rhenus in Latin. In 1929, Walter and Ida Noddack produced 1g of rhenium metal from 660 kg of Norwegian molybdenite.

Rhenium does not occur alone in nature in elemental form. It is found in trace quantities in a number of minerals such as columbite, gadolinite, molybdenite, tantalite, wolframite, and many platinum ores. Its average concentration in earth's crust is 0.0007mg/kg.

Rhenium is used in tungsten and molybdenum-based alloys. It is used for filaments for ion gages in mass spectrometers. Rhenium-tungsten alloys are used in thermocouples to measure temperatures up to 2,200°C. Rhenium wire is used in flash bulbs for photography. Rhenium compounds also are used as catalysts in hydrogenation and hydrocracking reactions in petroleum refining.

Physical Properties

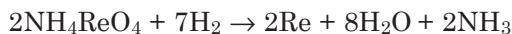
Metallic appearance in massive form, black to metallic color in powdered state or in electrodeposited form; hexagonal crystal system; density 20.53 g/cm³; hardness (Brinell) 250; melts at 3,180°C; vaporizes at 5,627°C (estimated); vapor pressure 4.6x10⁻⁵ torr at 2,500°C; electrical resistivity 19.14 microhm-cm; modulus of elasticity 67x10⁶ psi at 20°C; specific magnetic susceptibility 0.369x10⁻⁶; thermal neutron absorption cross section 86 barns/atom; superconductivity transition temperature 1.7°K; insoluble in water and hydrochloric acid; soluble in dilute nitric acid and hydrogen peroxide; slightly soluble in sulfuric acid.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	184.0 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	173.2 kcal/mol
S° (cry)	8.81 cal/deg mol
S° (gas)	45.13 cal/deg mol
C_p (cry)	6.09 cal/deg mol
C_p (gas)	4.97 cal/deg mol
Thermal conductivity (at 25°C)	0.480 W/cm/K
ΔH_{fus}	14.45 kcal/mol
Coefficient of linear expansion (20–1,000°C)	6.6–6.8x10 ⁻⁶ /°C

Production

Rhenium is usually recovered from the molybdenite ore, MoS₂. Such ores contain rhenium in concentrations ranging from 0.002 to 0.02%. The ore is roasted to produce flue dusts and effluent gases that contain rhenium and that serve as a raw material in making rhenium. Flue dusts and gases are leached and scrubbed with water. Rhenium oxide, Re₂O₇ and anhydride of perrhenic acid, HReO₄, dissolve in water. The solution becomes acidic because of perrhenic acid. The solution is treated with solid potassium chloride. This precipitates potassium perrhenate, KReO₄, which is purified by repeated crystallization. At the boiling point of water, the solubility of potassium perrhenate is about 14g/100g and at ordinary temperatures, it is below 1g/100g. Thermal dissociation of potassium perrhenate in the presence of hydrogen at elevated temperatures forms rhenium. Instead of potassium salt of perrhenic acid, the equivalent ammonium salt can be used. Ammonium perrhenate is heated with pure dry hydrogen at 700 to 800°C:



Rhenium is obtained as a metal powder. It is cooled to ambient temperature under a stream of nitrogen. The metal powder also may be pressed into bars in vacuum at 1,200°C.

Reactions

In compact or massive form, rhenium is stable at ordinary temperatures. When heated in oxygen or air at 350°C or above, it oxidizes to yellow heptoxide, Re_2O_7 . Rhenium also forms two other oxides, the red trioxide, ReO_3 , and the black dioxide, ReO_2 .

Rhenium reacts with all halogens including iodine to yield halides in several valence states from +1 to +6. Such halides include dark red hexagonal trichloride, ReCl_3 , dark green pentachloride, ReCl_5 , green hexafluoride, ReF_6 , and the greenish black crystalline tribromide, ReBr_3 .

The metal forms a dimeric pentacarbonyl $[\text{Re}(\text{CO})_5]_2$ which decomposes at 250°C. Also, it forms a yellow rhombohedral pentacarbonyl iodide, $\text{ReI} \cdot 5\text{CO}$, soluble in benzene and which decomposes at 400°C.

Rhenium forms two sulfides when heated with sulfur. These are the disulfide, obtained as black leaflets, having formula ReS_2 and a density 7.51 g/cm³ and the heptasulfide, Re_2S_7 , a black powdery material of density 4.87 g/cm³.

Rhenium is attacked by neither hydrochloric acid nor by cold sulfuric or hydrofluoric acid. However, oxidizing acids, such as nitric acid or hot sulfuric acid, vigorously react with the metal forming perrhenic acid, HReO_4 . The metal is oxidized by hydrogen peroxide in ammoniacal solution forming ammonium perrhenate, NH_4ReO_4 .

Rhenium combines with phosphorus, arsenic, silicon, selenium, and tellurium at elevated temperatures forming binary compounds. The metal, however, is stable in hydrogen and nitrogen at high temperatures.

Analysis

Rhenium can be analyzed by various instrumental techniques that include flame-AA, ICP-AES, ICP-MS, as well as x-ray and neutron activation methods. For flame-AA analysis the metal, its oxide, or other insoluble salts are dissolved in nitric acid or nitric-sulfuric acids, diluted, and aspirated directly into nitrous oxide-acetylene flame. Alternatively, rhenium is chelated with 8-hydroxyquinoline, extracted with methylisobutyl ketone and measured by flame-AA using nitrous oxide-acetylene flame.

RHODIUM

[7440-16-6]

Symbol Rh; atomic number 45; atomic weight 102.906; a Group VIII (Group 9) noble metal placed between cobalt and iridium; electron configuration $[\text{Kr}]4d^85s^1$; valence states +2, +3, +4, +5, +6; most stable valence state +3; atomic radius 1.34Å; ionic radius Rh^{3+} , 0.67Å (CN 6); standard electrode potential, $\text{Rh}^{3+} + 3e^- \leftrightarrow \text{Rh}$, $E^\circ = 0.578\text{V}$; one naturally-occurring isotope, Rh-103; twenty-five artificial radioactive isotopes in the mass range 92-102, 104-117; the longest-lived radioisotope, Rh-101, $t_{1/2}$ 3.3 year.

History, Occurrence, and Uses

Rhodium was discovered by W. H. Wollaston in 1803-04 in the aqua regia

extract of native platinum. After removal of platinum as diammonium platinum hexachloride, $(\text{NH}_4)_2\text{PtCl}_6$, from the aqua regia extract, the resulting filtrate contained two new metals, palladium and rhodium. The element was named rhodium, derived from the Greek word *rhodon* for the beautiful rose color of its chloro salt and its aqueous solution.

Rhodium occurs in nature in trace quantities, always associated with other platinum metals. It is found in native form. Its average abundance in the earth's crust is estimated to be 1mg/kg. Rhodium is used as a precious metal for making jewelry and decorative. Other important applications of this metal or its compounds are in making glass for mirrors or filtering light; in catalytic reactions to synthesize a number of products; as an alloying element for platinum; as a hardening agent for platinum and palladium at high temperatures; in electrical contact plates in radio- and audio-frequency circuits. Rhodium alloyed with platinum is used in thermocouples. A 10% Rh-Pt alloy was introduced by LeChatelier in 1885 for use in thermocouples. Also, rhodium alloys are used in laboratory crucibles, electrodes, optical instruments, furnace linings, and making glass fibers.

Physical Properties

Grayish-white metal; face-centered cubic crystals; density 12.41 g/cm³; hardness, annealed 100-120 Vickers units; melts at 1,964°C; vaporizes at 3,695°C; electrical resistivity 4.33 microhm-cm at 0°C; tensile strength, annealed 50 tons/in²; Young's modulus, annealed 2.3×10^4 tons/in²; magnetic susceptibility 0.99×10^{-6} cm³/g; thermal neutron absorption cross section 156 barns; insoluble in water; soluble in concentrated sulfuric or hydrochloric acid under boiling conditions; the metal in massive form is slightly soluble in aqua regia, but in small quantities or in thin plates it partially dissolves in aqua regia; forms solid solutions with platinum, palladium and iridium.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	133.1 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	122.1 kcal/mol
S° (cry)	7.53 cal/deg mol
S° (gas)	44.4 cal/deg mol
C_p (cry)	5.97 cal/deg mol
C_p (gas)	5.02 cal/deg mol
ΔH_{fus}	5.15 kcal/mol
Coefficient of linear expansion (20–100°C)	$8.3 \times 10^{-6}/^\circ\text{C}$
Thermal conductivity (0–100°C)	1.50 W/cmK

Reactions

At ordinary temperatures rhodium is stable in air. When heated above 600°C, it oxidizes to Rh_2O_3 , forming a dark oxide coating on its surface. The gray crystalline sesquioxide has a corundum-like crystal structure. The sesquioxide, Rh_2O_3 , decomposes back to its elements when heated above

1,100°C. However, on further heating the metal starts to lose its weight similar to platinum, probably due to loss of its volatile oxide RhO_2 dissolved in the metal. The molten metal readily absorbs gaseous oxygen.

The metal in powder form absorbs hydrogen when heated. When heated with carbon monoxide under pressure rhodium forms carbonyl, $\text{Rh}_4(\text{CO})_{12}$.

The metal combines with halogens at elevated temperatures. When heated with fluorine at 500 to 600°C, it forms a trifluoride, RhF_3 , a red rhombohedral crystalline powder insoluble in water, dilute acids, or alkalis. Also, a blue tetrafluoride, RhF_4 , is formed as a minor product. When heated with chlorine gas above 250°C, the brown-red trichloride, RhCl_3 , forms. It is hygroscopic, decomposing at 450°C.

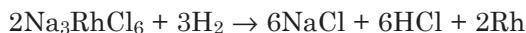
Rhodium is attacked by fused caustic soda or caustic potash. Also, fused sodium or potassium cyanide and sodium bisulfate attack the metal.

Recovery

The recovery of rhodium from the raw ores usually involves a series of lengthy steps. Rhodium may be obtained as one of the by-products from refining nickel by the Monod process. In this process the residue from refining nickel is leached with acid to form concentrates of the precious metals. Also, rhodium and other noble metals are derived from the anode slimes that accumulate in the electrolytic refining of copper and nickel. The precious metal concentrates obtained from such nickel refining are first treated with acids as appropriate to remove base metals. The solution is filtered and the precious metals in the residue are separated by treatment with aqua regia. While gold, platinum and palladium dissolve in aqua regia, rhodium remains mostly undissolved along with ruthenium, osmium, iridium, and silver. This residue, containing rhodium, is smelted with a mixture of lead carbonate, soda ash, borax, and carbon to produce slag. The smelting converts lead to an alloy that contains silver and precious metals. The alloy is treated with dilute nitric acid. Silver passes into the solution as soluble silver nitrate. The insoluble residue containing rhodium and other noble metals is fused with sodium bisulfate at 500°C in a silica vessel. Rhodium is converted to its water-soluble sulfate and separated from other noble metals that remain in insoluble residue when the fused mass is treated with water. The insoluble residue is filtered from the aqueous solution of rhodium sulfate. The solution is treated with caustic soda to precipitate rhodium as its hydroxide, $\text{Rh}(\text{OH})_3$. The hydroxide is washed and dissolved in hydrochloric acid. Impurity metals are removed by precipitation in the presence of nitrite. Addition of cobalt nitrite forms a nitrite complex of rhodium, $\text{CoRh}(\text{NO}_2)_6$, which remains in solution over a wide range of pH. Impurity metals are precipitated as their hydrous oxides under varying pH conditions. After the removal of impurity metals, ammonia is added to the solution whereupon rhodium precipitates as ammonium hexanitrorhodite, $(\text{NH}_4)_3\text{Rh}(\text{NO}_2)_6$. This complex is dissolved in hydrochloric acid. The solution containing chlororhodite, RhCl_6^{3-} , is passed through a column of cation exchange resin to remove trace impurity metals, such as lead, copper and iron. Boiling purified chlororhodite solution with formic acid precipitates rhodium black. This is reduced with hydrogen to form

high purity rhodium powder.

Wollaston's earliest method involved recovery of rhodium from native platinum. Pt was digested with aqua regia. Rhodium in bulk form is slightly soluble in aqua regia. However, when present as a minor constituent in platinum alloys, the metal may be extracted with aqua regia. Platinum was precipitated from aqua regia extract as ammonium hexachloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$. Addition of mercurous cyanide, $\text{Hg}_2(\text{CN})_2$, to the filtrate separated palladium as yellow palladium cyanide, $\text{Pd}(\text{CN})_2$. Excess mercurous cyanide in the remaining solution was decomposed by evaporating the solution with hydrochloric acid. The residue was treated with ethanol. A dark red solid residue that remained after alcohol treatment was a double chloride, sodium chlororhodite, $\text{Na}_3\text{RhCl}_6 \cdot 18\text{H}_2\text{O}$. Heating this rhodium complex with hydrogen decomposed the double chloride forming sodium chloride, hydrogen chloride and rhodium metal:



Sodium chloride was removed by leaching with water. Rhodium powder was left as residue.

Analysis

Rhodium may be analyzed by flame atomic absorption spectrophotometry using the direct air-acetylene flame method. The metal, its oxide and insoluble salts may be solubilized by digesting with sulfuric acid–hydrochloric acid mixture. Rhodium also may be analyzed by ICP-AES and ICP/MS techniques. ICP/MS is the most sensitive method. Also, it may be analyzed by neutron activation analysis.

RHODIUM CHLORIDE

[10049-07-7]

Formula: RhCl_3 ; MW 209.26; forms a trihydrate $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$

Synonyms: rhodium trichloride; rhodium(III) chloride

Uses

Rhodium chloride is used to prepare other rhodium salts.

Physical Properties

Brownish–red powder; deliquescent; decomposes on heating at 450 to 500°C; sublimes at 800°C; insoluble in water, water-solubility, however, depends on the method of preparation; soluble in alkali hydroxide or cyanide solutions; soluble in aqua regia

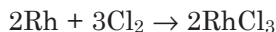
The trihydrate is a dark red powder; deliquescent; loses water at 100°C; very soluble in water; soluble in alcohol and hydrochloric acid; insoluble in ether.

Thermochemical Properties

$$\Delta H_f^\circ \quad -71.5 \text{ kcal/mol}$$

Preparation

Rhodium trichloride is prepared by heating rhodium with chlorine gas at 250°C:



Also, the chloride salt may be obtained by treating the yellow hydrous oxide, $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, with hydrochloric acid. The solution is carefully evaporated to form a dark red and water-soluble salt, rhodium trichloride tetrahydrate, $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$. Heating the tetrahydrate in a stream of hydrogen chloride gas at 180°C forms the anhydrous salt, RhCl_3 .

Analysis

Elemental composition: Rh 49.17%, Cl 50.83%. Rhodium is analyzed in an aqueous solution (or after dissolving in water) by AA or other techniques. Insoluble chloride is extracted with aqua regia, diluted, and analyzed to determine the rhodium content using various instrumental techniques. The chloride may be decomposed at elevated temperatures and liberated chlorine identified by color and other physical properties. Chlorine may be measured quantitatively by dissolving in an acidified solution of potassium iodide and titrating liberated iodine with a standard solution of sodium thiosulfate, using starch indicator.

RHODIUM SESQUIOXIDE

[12036-35-0]

Formula Rh_2O_3 ; MW 253.81; forms tri- and pentahydrates, $\text{Rh}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Synonym: rhodium(III) oxide

Uses

Rh_2O_3 is used to make rhodium metal and its various salts. Also, the oxide is a catalyst for hydrogenation.

Physical Properties

Gray crystalline solid or amorphous powder; corundum-type structure; density 8.20 g/cm³; decomposes at about 1,100 to 1,150°C; insoluble in water, acids, or aqua regia.

The pentahydrate $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is a yellow precipitate; soluble in acids; partially dissolves in hot water; ignites to form anhydrous oxide.

The trihydrate $\text{Rh}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is a black precipitate; insoluble in acids.

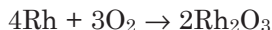
Thermochemical Properties

$$\Delta H_f^\circ \quad -82.0 \text{ kcal/mol}$$

C_p 24.8 cal/deg mol

Preparation

Rhodium sesquioxide is obtained by heating rhodium metal to red heat in air.



Alternatively, Rh_2O_3 may be prepared by igniting rhodium nitrate, $\text{Rh}(\text{NO}_3)_3$.

Treating the sesquioxide with alkali first forms a yellow precipitate of pentahydrate, $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, soluble in acid and excess alkali. In excess alkali a black precipitate of trihydrate, $\text{Rh}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is obtained. The trihydrate is insoluble in acids.

Analysis

Elemental composition (Rh_2O_3): Rh 81.09%, O 18.91%. The oxide may be solubilized by treatment with alkali to form hydrated oxide, which may be dissolved in acid and diluted for analysis of rhodium metal by AA or ICP. The oxide may be characterized by x-ray diffraction, physical properties, and reaction with strong alkali to form yellow precipitate of pentahydrate, and in excess alkali a black precipitate of the trihydrate.

RUBIDIUM

[7440-17-7]

Symbol Rb; atomic number 37; atomic weight 85.468; a Group I (Group 1) alkali metal element; electron configuration $[\text{Kr}] 5s^1$; valence +1; atomic radius 2.43Å; ionic radius, Rb^+ 1.48Å; atomic volume 55.9 cc/g-atom at 20°C; ionization potential 4.177 V; standard electrode potential $\text{Rb}^+ + e^- \leftrightarrow \text{Rb}$, $E^\circ = -2.98\text{V}$; two naturally-occurring isotopes, Rb-85 (72.165%) and Rb-87 (27.835%); Rb-87 radioactive, a beta emitter with a half-life 4.88×10^{10} year; twenty-seven artificial radioactive isotopes in the mass range 74–84, 86, 88–102.

History, Occurrence, and Uses

Rubidium was discovered in 1861 by Kirchoff and Bunsen. They observed new lines in the dark red spectral region of a sample extract of mineral lepidolite. The element got its name from the Latin word *rubidus*, which means dark red. Bunsen later succeeded in preparing metallic rubidium in low yield by heating rubidium hydrogen tartrate with carbon. The metal was obtained in higher yield by Hevesy and later by Beketov, Hevesy electrolyzing a melt of rubidium hydroxide and Beketov reducing the hydroxide with aluminum at red heat.

Rubidium is widely distributed in nature. Its abundance in the earth's crust is estimated to be 90 mg/kg. Rubidium occurs at trace levels in many potassium minerals. Often it is associated with cesium. Some rubidium-con-

taining minerals are lepidolite, leucite, petalite, feldspars, pollucite, beryl, and amazonite. The metal is never found as a major constituent in any mineral. Rubidium also occurs in many rocks such as basalts, granites and clay shales. Rubidium is found in seawater at an average concentration of 0.12 mg/L.

Rubidium metal and its salts have very few commercial applications. They are used in research involving magnetohydrodynamics and thermoionic experiments. Rubidium is used in photocells. The metal also is a getter of oxygen in vacuum tubes. The beta-emitter rubidium -87 is used to determine age of some rocks and minerals. Radioisotopes of rubidium have been used as radioactive tracers to trace the flow of blood in the body. The iodide salt treats goiters. Rubidium salts are in pharmaceuticals as soporifics, sedatives, and for treating epilepsy.

Physical Properties

Silvery-white metal; body-centered cubic crystals; ductile; soft and very light (the fourth lightest metallic element); Mohs hardness 0.3; density 1.522 g/cm³ at 18°C; melts at 39.3°C; density of the liquid metal 1.472 g/mL at 39°C; vaporizes at 689°C producing a blue vapor; vapor pressure 1 torr at 294°C and 10 torr at 387°C; electrical resistivity 11.6 microhm-cm at 0°C and 13.1 mirohm-cm at 25°C; viscosity 0.484 centipoise at 100°C; magnetic susceptibility 0.09×10^{-6} cgs units at 18°C; thermal neutron absorption cross section 0.73 barns; reacts violently with water

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$\Delta H_f^\circ(\text{gas})$	19.34 kcal/mol
$\Delta G_f^\circ(\text{gas})$	12.69 kcal/mol
$S^\circ(\text{cry})$	18.36 cal/deg mol
$S^\circ(\text{gas})$	40.66 cal/deg mol
$C_p(\text{cry})$	7.43 cal/deg mol
$C_p(\text{gas})$	4.97 cal/deg mol
ΔH_{fus}	0.52 kcal/mol
Thermal conductivity (at 27°C)	0.582 W/cmK
Coefficient of linear expansion (at 20°C)	$90 \times 10^{-6}/^\circ\text{C}$

Production

Rubidium is recovered from its ore lepidolite or pollucite. Mineral lepidolite is a lithium mica having a composition: $\text{KRbLi}(\text{OH}, \text{F})\text{Al}_2\text{Si}_3\text{O}_{10}$. The ore is opened by fusion with gypsum (potassium sulfate) or with a mixture of barium sulfate and barium carbonate. The fused mass is extracted with hot water to leach out water-soluble alums of cesium, rubidium, and potassium. The solution is filtered to remove insoluble residues. Alums of alkali metals are separated from solution by fractional crystallization. Solubility of rubidium alum or rubidium aluminum sulfate dodecahydrate, $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ falls between potassium and cesium alum.

Alternatively, the mineral is opened by prolonged heating with sulfuric

acid. Often calcium fluoride (fluorspar) is added for removal of silicon. Alkali metals are converted into water-soluble sulfates. After filtering residual solid, the solution is treated with ammonium or potassium carbonate or carbon dioxide. Lithium precipitates as lithium carbonate. Alkali metal carbonates are converted back to alums and separated by fractional crystallization.

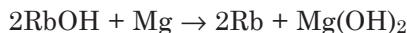
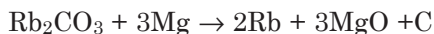
Rubidium alum obtained by either method above is decomposed by treatment with alkali solutions for removal of aluminum and sulfate. Aluminum is precipitated as aluminum hydroxide. Addition of barium hydroxide to the filtrate removes sulfate, precipitating barium sulfate. Evaporation of the solution crystallizes rubidium as hydroxide.

Rubidium also may be recovered by the chlorostannate method. In this method the alkali metal carbonate solution obtained from the mixed alum is treated with carbon dioxide. Most potassium is precipitated as bicarbonate, KHCO_3 . Addition of hydrochloric acid converts the carbonates to chlorides. The chlorides are converted to chlorostannates by carefully adding stoichiometric quantities of stannic chloride at pH just below 7:



Cesium chlorostannate, Cs_2SnCl_6 , more insoluble than the rubidium salt, precipitates before any rubidium starts to precipitate. Under such controlled addition of stannic chloride, potassium chloride remains in solution in chloride form. Rubidium chlorostannate complex, on thermal decomposition, forms rubidium chloride, RbCl .

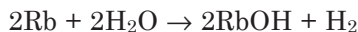
Rubidium metal may be obtained from its carbonate, hydroxide or chloride by reduction with magnesium or calcium at high temperatures in the presence of hydrogen:



Rubidium is a flammable solid. It is stored in dry hexane, isooctane or other saturated hydrocarbon liquids. Alternatively, the metal may be packaged and stored in well-sealed borosilicate glass ampules or stainless-steel containers under vacuum or an inert atmosphere.

Reactions

Rubidium is a highly reactive metal, more reactive than sodium or potassium. Most reactions are similar to sodium or potassium (see Potassium). The metal ignites spontaneously in air forming oxides. It is coated rapidly with a gray-blue oxide film. It forms four oxides, Rb_2O , Rb_2O_2 , Rb_2O_3 , and Rb_2O_4 . It reacts violently with water to form rubidium hydroxide, RbOH :



Reaction with dilute mineral acids can proceed with explosive violence, releasing hydrogen.

Rubidium combines with hydrogen and nitrogen forming hydride, RbH and nitride, Rb_3N , respectively.

Analysis

Rubidium and its salts may be analyzed by flame AA, flame photometric and ICP/AES methods. Rb metal imparts a deep red color to flame.

Hazard

As a highly reactive metal, its contact with water or acids can produce violent reactions. Skin contact can cause serious burns.

RUBIDIUM CARBONATE

[584-09-8]

Formula Rb_2CO_3 ; MW 230.945; readily forms a monohydrate, $\text{Rb}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

Uses

Rubidium carbonate is used in special glass and in fiber optics. It enhances stability and durability of glass, reducing its conductivity. It also is used in the preparation of Rb metal and other rubidium salts.

Physical Properties

Colorless crystals or white powder; monoclinic structure; very hygroscopic; melts at 837°C ; decomposes above 900°C ; very soluble in water

Thermochemical Properties

ΔH_f°	-271.5 kcal/mol
ΔG_f°	-251.2 kcal/mol
S°	43.3 cal/deg mol
C_p	28.1 cal/deg mol

Preparation

Rubidium carbonate is an intermediate in recovery of rubidium from lepidolite. The mineral, on prolonged heating with concentrated sulfuric acid, converts to alums.

The mixed alum solution, on treatment with ammonia or potassium carbonate, forms carbonates of potassium, rubidium and cesium. Rubidium carbonate is separated from other alkali metal carbonates by fractional crystallization (see Rubidium)

The carbonate salt also may be obtained by passing carbon dioxide through a solution of rubidium hydroxide in a fluorocarbon or nickel container. The solution is evaporated to yield the product carbonate.

Also, the salt may be prepared by adding ammonium carbonate to a solution of rubidium hydroxide. The solution is evaporated to dryness to expel ammonia.

Analysis

Rubidium may be analyzed in an aqueous solution of rubidium carbonate by AA, ICP-AES or other methods (see Rubidium). Carbonate anion, CO_3^{2-} may be measured quantitatively by ion chromatography. Additionally, CO_3^{2-} may be tested by treating Rb salt with a dilute acid. Liberation of CO_2 with effervescence that turns lime water milky is a qualitative test.

RUBIDIUM CHLORIDE

[7791-11-9]

Formula RbCl ; MW 120.91

Uses

Rubidium chloride is used in preparing rubidium metal and many rubidium salts. Also, it is used in pharmaceuticals as an antidepressant and as a density-gradient medium for centrifugal separation of viruses, DNA, and large particles. Other applications are as an additive to gasoline to improve its octane number and as a catalyst.

Physical Properties

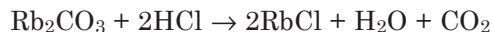
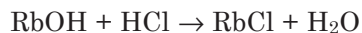
Colorless cubic crystals; refractive index 1.493 at 35°C ; density 2.80 g/cm^3 at 25°C ; density of liquid melt 2.088 g/mL at 750°C ; melts at 718°C ; vaporizes at $1,390^\circ\text{C}$; readily dissolves in water, solubility 77 g/100mL at 0°C and 139 g/100mL at 100°C ; sparingly soluble in methanol, 1.41g/100mL at 25°C .

Thermochemical Properties

ΔH_f°	-104.05 kcal/mol
ΔG_f°	-97.5 kcal/mol
S°	22.9 cal/deg mol
C_p	12.5 cal/deg mol

Preparation

Rubidium chloride is prepared by adding hydrochloric acid to a solution of rubidium carbonate or hydroxide. The solution is evaporated to obtain well-defined colorless cubic crystals of rubidium chloride

**Analysis**

Elemental analysis: Rb 70.68%, Cl 29.32%. Aqueous solution of rubidium chloride may be analyzed for rubidium by AA or ICP and for the chloride anion by ion chromatography or titration with a standard solution of silver

nitrate using potassium chromate as indicator.

RUBIDIUM HYDROXIDE

[1310-82-3]

Formula RbOH; MW 102.475

Synonym: rubidium hydrate

Uses

Rubidium hydroxide is used as a catalyst in oxidative chlorination. It also may be used as a powerful base, stronger than caustic potash, in many preparative reactions. The compound holds promising applications as an electrolyte in storage batteries for use at low temperatures.

Physical Properties

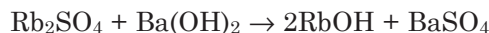
Grayish-white orthogonol crystals; hygroscopic; density 3.2 g/cm³; melts at 301°C; very soluble in water (100 g/100 mL at 15°C), the solution highly alkaline; soluble in ethanol.

Thermochemical Properties

$$\Delta H_f^\circ \quad -96.6 \text{ kcal/mol}$$

Preparation

Rubidium hydroxide may be obtained as an intermediate in recovering rubidium metal from mineral lepidolite (see Rubidium). In the laboratory it may be prepared by adding barium hydroxide to a solution of rubidium sulfate. The insoluble barium sulfate is separated by filtration:



Preparation should be in nickel or silver containers because rubidium hydroxide attacks glass. The solution is concentrated by partial evaporation. The commercial product is usually a 50% aqueous solution.

Reactions

Rubidium hydroxide is a stronger base than caustic soda or caustic potash. Its reactions are similar to theirs. Neutralization occurs with acids. Rubidium hydroxide absorbs carbon dioxide forming rubidium carbonate.

Analysis

Rubidium may be analyzed by various instrumental methods (see Rubidium). The strength of solution may be measured by titration against a standard solution of strong acid using a color indicator or a potentiometer.

Toxicity

The compound or its aqueous solution is highly corrosive. Skin or eye con-

tact can cause serious injury.

RUBIDIUM SULFATE

[7488-54-2]

Formula Rb_2SO_4 ; MW 267.00

Physical Properties

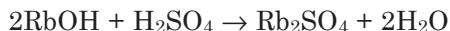
White orthogonal crystal; density 3.6 g/cm^3 ; melts at $1,050^\circ\text{C}$; very soluble in water, 36 g/100g at 0°C and 82 g/100g at 100°C .

Thermochemical Properties

ΔH_f°	-343.1 kcal/mol
ΔG_f°	-314.7 kcal/mol
S°	47.2 cal/deg mol
C_p	32.1 cal/deg mol

Preparation

Rubidium sulfate can be prepared by neutralization of a solution of rubidium hydroxide or carbonate with sulfuric acid:



Alternatively, Rb sulfate may be obtained by treating a hot solution of rubidium aluminum sulfate (rubidium alum) with ammonia solution. Aluminum hydroxide precipitates. The product mixture is filtered. The filtrate on evaporation crystallizes rubidium sulfate.

Analysis

An aqueous solution of the salt may be analyzed for rubidium by AA, ICP-AES and flame photometry, and for sulfate anion by ion chromatography. Rb sulfate in solution also may be measured by gravimetry after adding barium chloride to precipitate sulfate as barium sulfate, BaSO_4 .

RUTHENIUM

[7440-18-8]

Symbol: Ru; atomic number 44; atomic weight 101.07; a Group VIII (Group 9) noble metal; electron configuration $[\text{Kr}]4d^75s^1$; valence states 0, +1, +2, +3, +4, +5, +6, +7, +8; most stable valence states +2, +3, +4; atomic radius $1.34\text{\AA}$; ionic radius, Ru^{8+} $0.36\text{\AA}$ (for a coordination number 8); seven naturally-occurring stable isotopes: Ru-96 (5.53%), Ru-98 (1.89%), Ru-99 (12.71%), Ru-100 (12.61%), Ru-101 (17.01%), Ru-102 (31.62%), Ru-104 (18.72%); twenty artifi-

cial radioactive isotopes in the mass range 89-95, 97, 103, 105-115; longest-lived isotope Ru-106, $t_{1/2}$ 1.02 year; shortest-lived isotope Ru-114, $t_{1/2}$ 0.57 second

History, Occurrence, and Uses

Ruthenium was recognized as a new element by G.W. Osann in 1828. He found it in insoluble residues from aqua regia extract of native platinum from alluvial deposits in the Ural mountains of Russia. He named it *Ruthen* after the Latin name *Ruthenia* for Russia. The discovery of this element, however, is credited to Klaus who in 1844 found that Osann's ruthenium oxide was very impure and isolated pure Ru metal from crude platinum residues insoluble in aqua regia.

Ruthenium occurs in nature natively, found in minor quantities associated with other platinum metals. Its abundance in the earth's crust is estimated to be 0.001 mg/kg, comparable to that of rhodium and iridium.

Ruthenium alloyed to platinum, palladium, titanium and molybdenum have many applications. It is an effective hardening element for platinum and palladium. Such alloys have high resistance to corrosion and oxidation and are used to make electrical contacts for resistance to severe wear. Ruthenium-palladium alloys are used in jewelry, decorations, and dental work. Addition of 0.1% ruthenium markedly improves corrosion resistance of titanium. Ruthenium alloys make tips for fountain pen nibs, instrument pivots, and electrical goods. Ruthenium catalysts are used in selective hydrogenation of carbonyl groups to convert aldehydes and ketones to alcohols.

Physical Properties

Hard silvery-white metal; hexagonal close-packed crystal structure; density 12.41 g/cm³ at 20°C; melts at 2,334°C; vaporizes at 4,150°C; electrical resistivity 7.1 microhm-cm at 0°C; hardness (annealed) 200-350 Vickers units; Young's modulus 3.0×10^4 tons/in²; magnetic susceptibility 0.427 cm³/g; thermal neutron absorption cross section 2.6 barns; insoluble in water, cold or hot acids, and aqua regia; can be brought into aqueous phase by fusion of finely divided metal with alkaline hydroxides, peroxides, carbonates and cyanides.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$\Delta H_f^\circ(\text{gas})$	153.6 kcal/mol
$\Delta G_f^\circ(\text{cry})$	0.0
$\Delta G_f^\circ(\text{gas})$	142.4 kcal/mol
$S^\circ(\text{cry})$	6.82 cal/deg mol
$S^\circ(\text{gas})$	44.55 cal/deg mol
$C_p(\text{cry})$	5.75 cal/deg mol
$C_p(\text{gas})$	5.14 cal/deg mol
ΔH_{fus}	9.22 cal/deg mol
Thermal conductivity (at 27°C)	1.17 W/cmK
Coefficient of linear expansion (at 25°C)	$6.4 \times 10^{-6}/^\circ\text{C}$

Production

Ruthenium is derived from platinum metal ores. Method of production depends on the type of ore. However, the extraction processes are similar to those of other noble metals (see Platinum, Rhodium and Iridium). Ruthenium, like Rhodium, may be obtained from accumulated anode sludges in electrolytic refining of nickel or copper from certain types of ores. Also, residues from refining nickel by Mond carbonyl process contain ruthenium and other precious metals at very low concentrations. The extraction processes are very lengthy, involving smelting with suitable fluxes and acid treatments.

Metals, such as gold, platinum, and palladium, are separated by digesting refining residues with aqua regia. These metals are soluble in aqua regia, leaving ruthenium, rhodium, iridium, osmium, and silver in the insoluble residue.

The treatment of this insoluble residue may vary. In one typical process, residue is subjected to fusion with sodium peroxide. Ruthenium and osmium are converted to water-soluble sodium ruthenate and osmate, which are leached with water. The aqueous solution is treated with chlorine gas and heated. The ruthenate and the osmate are converted to their tetroxides. Ruthenium tetroxide is distilled out and collected in hydrochloric acid. The tetroxide is converted into ruthenium chloride. Traces of osmium are removed from ruthenium chloride solution by boiling with nitric acid.

Nitric acid converts osmium to volatile osmium tetroxide but forms a nitrosyl complex with ruthenium that remains in the solution. After removal of trace osmium, the solution is treated with ammonium chloride. This precipitates ruthenium as crystals of ammonium chlororuthenate, NH_4RuCl_6 . The precipitate is washed, dried, and ignited to form ruthenium black. This is reduced with hydrogen at $1,000^\circ\text{C}$ to form very pure ruthenium powder.

Reactions

When heated in air at 500 to 700°C , ruthenium converts to its dioxide, RuO_2 , a black crystalline solid of rutile structure. A trioxide of ruthenium, RuO_3 , also is known; formed when the metal is heated above $1,000^\circ\text{C}$. Above $1,100^\circ\text{C}$ the metal loses weight because trioxide partially volatilizes.

Ruthenium also forms a tetroxide, RuO_4 , which, unlike osmium, is not produced by direct union of the elements.

Halogens react with the metal at elevated temperatures. Fluorine reacts with ruthenium at 300°C forming colorless vapors of pentafluoride, RuF_5 , which at ordinary temperatures converts to a green solid. Chlorine combines with the metal at 450°C to form black trichloride, RuCl_3 , which is insoluble in water. Ru metal at ambient temperature is attacked by chlorine water, bromine water, or alcoholic solution of iodine.

Ruthenium is stable in practically all acids including aqua regia. Fusion with an alkali in the presence of an oxidizing agent forms ruthenate, RuO_4^{2-} and perruthenate, RuO_4^- .

When finely-divided Ru metal is heated with carbon monoxide under 200 atm pressure, ruthenium converts to pentacarbonyl, $\text{Ru}(\text{CO})_5$, a colorless liquid that decomposes on heating to diruthenium nonacarbonyl, $\text{Ru}_2(\text{CO})_9$, a

yellow crystalline solid.

Ruthenium reacts with cyclopentadiene in ether to form a sandwich complex, a yellow crystalline compound, bis(cyclopentadiene) ruthenium(0), also known as ruthenocene.

Analysis

Ruthenium and its compounds are analyzed by flame AA method using nitrous oxide-acetylene flame. ICP-AES, ICP/MS, and neutron activation analysis are also applicable. The metal or its insoluble compounds may be solubilized by fusion with alkali and leached with water.

RUTHERFORDIUM

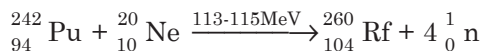
[53850-36-5]

Symbol Rf; atomic number 104; atomic weight 261; a man-made radioactive element; first transactinide element; a Group IV B (Group 4) element below hafnium in titanium subgroup; electron configuration [Rn]6d²7s²; valence +4

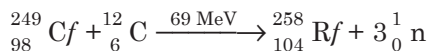
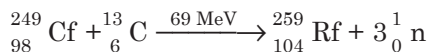
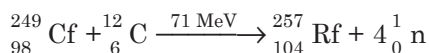
The element was discovered in 1964 by the scientists at the Joint Nuclear Research Institute at Dubna, USSR, by accelerating neon ions of 113 to 115 MeV energy. They obtained an isotope of this new element having mass 260. The group proposed the name Kurchatovium for this new element in honor of Soviet physicist Igor Kurchatov. Attempts to synthesize this element by Ghiorso and group at Berkeley, California by the above method were not successful. In 1969, Ghiorso and his team obtained three isotopes of element 104 by bombardment of Californium-249 with high energy carbon-12 and carbon-13. The isotopes had mass 257, 258 and 259. The element is currently named Rutherfordium in honor of Ernest Rutherford.

Synthesis

The element was prepared first by bombardment of plutonium-242 with high energy neon ions:



Rutherfordium-257, -258 and -259 were produced by Ghiorso and his group by bombarding californium-249 with high energy carbon-12 and carbon-13 isotopes:



The isotope Rf-257 has a half-life of 4.7 sec. It is an alpha-emitter decaying to nobelium-253. The isotopes Rf-258 and Rf-259 have the half-life of 12ms and 3.4 sec., respectively.

Rutherfordium is chemically similar to hafnium, the element above it in the same subgroup. The element has no commercial application.

SAMARIUM

[7440-19-9]

Symbol: Sm; atomic number 62; atomic weight 150.36; a lanthanide series inner transition element; a rare earth metal; electron configuration $[\text{Xe}]4f^66s^2$; partially-filled *f* orbitals; valence states +2, +3; atomic radius 1.804Å; ionic radius of Sm^{3+} 1.08Å (for coordination number 8); seven naturally-occurring isotopes: Sm-144 (3.11%), Sm-147 (15.02%), Sm-148 (11.31%), Sm-149 (13.81%), Sm-150 (7.41%), Sm-152 (26.72%), Sm-154 (22.72%); the isotopes 147, 148, 149 radioactive; twenty-two artificial radioactive isotopes in the mass range 131,133–143, 145–146, 151, 153, 155–160; longest-lived radioactive isotopes are naturally-occurring Sm-149, $t_{1/2}$ 10^{16} year and Sm-148, $t_{1/2}$ 7×10^{15} year; shortest-lived isotope Sm-131, $t_{1/2}$ 1.2 seconds

History, Occurrence, and Uses

The discovery of samarium is credited to Boisbaudran, who in 1879 separated its oxide, "samaria" from Mosander's "didymia," the mixture of rare earth oxides from which cerium and lanthanum were isolated earlier. Demarcay in 1901 first identified samaria to be a mixture of samarium and europium oxides. The element got its name from its mineral, samarskite. The mineral, in turn, was named in honor of the Russian mine official Col. Samarki.

Samarium occurs in nature widely distributed but in trace quantities, always associated with other rare earth metals. The two most important minerals are (i) monazite, which is an orthophosphate of thorium and the rare earths; and (ii) bastanasite, which is a rare earth fluocarbonate. The samarium content of these ores is about 2%, as oxide. It also is found in precambrian granite rocks, shales, and certain minerals, such as xenotime and basalt. Its abundance in the earth's crust is estimated to be 7.05 mg/kg.

Samarium salts are used in optical glass, capacitors, thermoionic generating devices, and in sensitizers of phosphors. The metal is doped with calcium fluoride crystals for use in lasers. It also is used along with other rare earths for carbon-arc lighting. Its alloys are used in permanent magnets.

Recovery

Samarium ore usually is digested with concentrated sulfuric or hydrochloric acid. The extraction process is similar to other lanthanide elements. Recovery of the metal generally consists of three basic steps. These are (1) opening the ore, (2) separation of rare earths first to various fractions and finally to their individual compounds, usually oxides or halides, and (3) reduc-

tion of the oxide or halide to pure metal. Although recovery of samarium involves mostly the same processes as other rare earth metals, the final reduction steps are quite different from most other metals. Commercial processes vary, depending on type and chemical nature of the ore, end product, purity desired, and cost. One such classical recovery process using monazite as the starting material is briefly mentioned below (Silvernail, W.L. Samarium. In *The Encyclopedia of Chemical Elements*, ed. C.A. Hampel, 1968. pp 616–620. New York: Reinhold.) At present, separation of rare earths is by methods based on ion exchange and solvent extraction.

The monazite sand is heated with sulfuric acid at about 120 to 170°C. An exothermic reaction ensues raising the temperature to above 200°C. Samarium and other rare earths are converted to their water-soluble sulfates. The residue is extracted with water and the solution is treated with sodium pyrophosphate to precipitate thorium. After removing thorium, the solution is treated with sodium sulfate to precipitate rare earths as their double sulfates, that is, rare earth sulfates-sodium sulfate. The double sulfates are heated with sodium hydroxide to convert them into rare earth hydroxides. The hydroxides are treated with hydrochloric or nitric acid to solubilize all rare earths except cerium. The insoluble cerium(IV) hydroxide is filtered. Lanthanum and other rare earths are then separated by fractional crystallization after converting them to double salts with ammonium or magnesium nitrate. The samarium-europium fraction is converted to acetates and reduced with sodium amalgam to low valence states. The reduced metals are extracted with dilute acid. As mentioned above, this fractional crystallization process is very tedious, time-consuming, and currently rare earths are separated by relatively easier methods based on ion exchange and solvent extraction.

Metallic samarium is obtained by heating the oxide, Sm_2O_3 with lanthanum turnings or cerium in slight excess amounts in a tantalum crucible under high vacuum. The metal is recovered by condensation of its vapors at 300 to 400°C. The metal cannot be obtained by reduction of its halides, SmF_3 or SmCl_3 , or by heating with calcium or barium. In such reduction, trihalides are reduced to dihalides, but not to the metal.

Physical Properties

Hard yellow metal; exhibits two crystals forms: an alpha form having a rhombohedral crystal structure at ordinary temperatures; the alpha form converts to a body-centered cubic beta form at 917°C; density 7.52 g/cm³ (alpha form) and 7.40 g/cm³ (beta form) melts at 1,074°C; vaporizes at 1,791°C; ignites in air at 150°C; electrical resistivity 94 microhm-cm at 25°C; thermal neutron absorption cross section 5,600 barns; insoluble in water; soluble in acid.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$\Delta H_f^\circ(\text{gas})$	49.4 kcal/mol
$\Delta G_f^\circ(\text{cry})$	0.0

$\Delta G_f^\circ(\text{gas})$	41.3 kcal/mol
$S^\circ(\text{cry})$	16.6 cal/deg mol
$S^\circ(\text{gas})$	43.7 cal/deg mol
$C_p(\text{cry})$	7.06 cal/deg mol
$C_p(\text{gas})$	7.26 cal/deg mol
ΔH_{fus}	2.06 kcal/mol
$\Delta H_{\text{subl}}(\text{at } 25^\circ\text{C})$	49.3 kcal/mol

Reactions

Samarium is stable in dry air at ordinary temperatures. However, it oxidizes in moist air forming an oxide coating. The metal ignites in air at about 150°C. It reacts with hydrogen, nitrogen, phosphorus, sulfur and carbon at elevated temperatures forming binary compounds. Samarium burns in halogen vapors at about 200°C forming halides.

Samarium reduces several metal oxides to metals. Such metal oxides include iron, zinc, lead, chromium, manganese, tin, and zirconium. When heated with carbon monoxide, it forms samarium oxide and carbon.

Samarium forms salts both in +3 and +2 oxidation states. The trivalent salts are more prevalent. Among the trivalent salts, the sesquioxide, Sm_2O_3 [12060-58-1], is commercially important. Other trivalent compounds include the pale yellow triclinic nitrate hexahydrate, $\text{Sm}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$, the yellow chromate octahydrate, $\text{Sm}_2(\text{CrO}_4)_3 \cdot 8\text{H}_2\text{O}$; the greenish yellow triclinic trichloride hexahydrate, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ [13456-55-9]; white crystalline oxalate decahydrate, $\text{Sm}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$; light yellow monoclinic sulfate octahydrate, $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ [13456-58-2]; violet orthorhombic molybdate, $\text{Sm}_2(\text{MoO}_4)_3$; and the pale yellow trihydroxide, $\text{Sm}(\text{OH})_3$.

The divalent compounds of samarium primarily are halides, the reddish-brown crystalline dichloride, SmCl_2 [13874-75-4]; the dark-brown diiodide, SmI_2 [32248-43-4]; and the dark brown dibromide, SmBr_2 [50801-97-3]. Samarium also forms a difluoride, SmF_2 [15192-17-3]. The trivalent salts of these halogens are more stable than their divalent counterparts.

Analysis

Samarium may be analyzed by spectrographic and spectrophotometric methods. In solution, the trivalent samarium shows sharp and intense absorption bands at 362.5, 347.5 and 402.0 nm. Trace analysis may be carried out most accurately by flame AA, ICP-AES, ICP/MS and neutron activation analysis. ICP/MS is the most sensitive method. The metal and its insoluble salts may be solubilized by digestion with acids and diluted appropriately for most instrumental measurements.

SAMARIUM SESQUIOXIDE

[12060-58-1]

Formula Sm_2O_3 ; MW 348.72

Synonyms: samarium(III) oxide, samarium oxide; samaria

Uses

Samarium sesquioxide is used in optical and infrared absorbing glass to absorb infrared radiation. Also, it is used as a neutron absorber in control rods for nuclear power reactors. The oxide catalyzes dehydration of acyclic primary alcohols to aldehydes and ketones. Another use involves preparation of other samarium salts.

Physical Properties

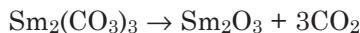
Yellowish-white powder; density 8.347g/cm³; insoluble in water; dissolves readily in mineral acids.

Thermochemical Properties

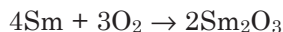
ΔH_f°	-435.7 kcal/mol
ΔG_f°	-414.6 kcal/mol
S°	36.1 cal/deg mol
C_p	27.4 cal/deg mol

Preparation

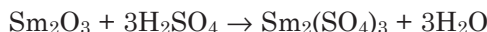
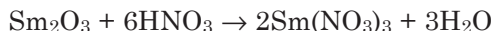
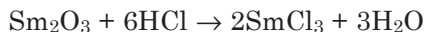
Samarium sesquioxide may be prepared by two methods; (1) thermal decomposition of samarium carbonate, hydroxide, nitrate, oxalate or sulfate:



or (2) by burning the metal in air or oxygen at a temperature above 150°C:

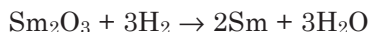
**Reactions**

Samarium sesquioxide dissolves in mineral acids, forming salts upon evaporation and crystallization:



Salts obtained upon crystallization are the hydrated salts, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

The oxide is reduced to metallic samarium by heating with a reducing agent, such as hydrogen or carbon monoxide, at elevated temperatures:



Analysis

Elemental composition: Sm 86.24%, O 13.76%. The oxide may be dissolved in a mineral acid, diluted, and analyzed by flame AA or ICP-AES. Also the oxide can be characterized nondestructively by x-ray diffraction.

SCANDIUM

[7440-20-2]

Symbol Sc; atomic number 21; atomic weight 44.956; a Group III B (Group 3) transition metal; electron configuration $[\text{Ar}]3d^14s^2$; valence state +3; atomic radius 1.62Å; ionic radius Sc^{3+} 0.75Å (for coordination number 6); ionization potential ($\text{Sc} \rightarrow \text{Sc}^{3+}$) 24.76 eV; one naturally-occurring isotope scandium-45; fifteen artificial radioactive isotopes in the mass range 40–44 and 46–55; the longest-lived radioisotope Sc-46, $t_{1/2}$ 83.8 days; shortest-lived isotope Sc-40, $t_{1/2}$ 0.18 second,

History, Occurrence, and Uses

The existence of scandium was predicted in 1871 by Mendeleev, who placed it under boron in Group III of his Periodic Table. He called it *ekaboron*. Five years later Lars Nilson of Sweden discovered this new element while examining the ore euxenite. Nilson named this element scandium after his homeland Scandinavia. Metallic scandium was prepared first by Fisher, Brunger, and Grieneisen in 1937 by an electrolytic process.

Scandium occurs in nature, very widely dispersed in low concentrations. It is found in most soils and numerous minerals in very minute quantities. The principal minerals are wolframite, euxenite, wiikite, bazzite, cassiterite, gadolinite, and thortveitite. Its abundance in the earth's crust is estimated to be 22 mg/kg. The element also has been detected in the sun and other stars.

The metal is used to produce high intensity lights. Its iodide is added to mercury vapor lamps to form very bright indoor lights. Radioactive scandium-46 is used as a tracer for crude oil.

Physical Properties

Silvery white metal; soft and light; turns slightly yellow when exposed to air; density 2.99 g/cm³; exhibits two allotropic modifications: a hexagonal close-packed structure stable up to 1,335°; transforms to body-centered cubic form above 1,335°C, having a density 3.19 g/cm³; melts at 1,541°C; vaporizes at 2,831°C; electrical resistivity 56.2×10^{-6} ohm-cm; thermal neutron absorption cross section 24 ± 1 barns; decomposes in water.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	90.3 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	80.3 kcal/mol
S° (cry)	8.28 cal/deg mol

$S^\circ(\text{gas})$	41.8 cal/deg mol
$C_p(\text{cry})$	6.10 cal/deg mol
$C_p(\text{gas})$	5.28 cal/deg mol
ΔH_{fus}	3.37 kcal/mol
Thermal conductivity(at 27°C)	0.158 W/cmK
Coefficient of linear expansion (at 25°C)	$10.2 \times 10^{-6}/^\circ\text{C}$

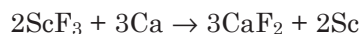
Recovery

Scandium mostly is extracted from its ore thortveitite, $(\text{Sc}, \text{Y})_2\text{Si}_2\text{O}_7$, which has the highest scandium content among the ores. The scandium content in this ore usually varies between 30 to 40% as Sc_2O_3 . The ore also contains about 46% SiO_2 , 9.5% heavy rare earths, 5% Al_2O_3 , 3% Fe_2O_3 , 1.5% light rare earths, and smaller amounts of oxides of manganese, calcium, magnesium, thorium, hafnium, and zirconium.

The ore thortveitite is crushed and powdered. It is mixed with a large excess of ammonium hydrogen fluoride and heated at about 400°C for several hours in a platinum container under a stream of dry air. Silica is converted to volatile silicon tetrafluoride and swept out with dry air. Scandium oxide is converted to scandium trifluoride, ScF_3 :



All other metals also are converted to their fluorides. The fluoride mixture is heated at 1,400°C in a tantalum crucible in an inert atmosphere. This produces a scandium-rich alloy phase constituting about 70% Sc and calcium fluoride slag:



Treatment with hydrochloric acid dissolves scandium and other metals. The solution is treated with sodium thiocyanate and extracted with ether. Scandium converted to its oxide Sc_2O_3 is separated from the solvent extract by ion exchange.

The ore thortveitite may be cracked by fusion with sodium carbonate or by heating with hydrofluoric acid. In a series of steps, scandium is precipitated as hydroxide or oxalate, which on thermal decomposition forms lower yield of oxide. This recovery, however, is tedious and is now obsolete.

Scandium also is obtained as a by-product of processing uranium ores, although they contain only traces of the metal.

In most recovery processes, scandium oxide is converted to its fluoride salt. The fluoride salt is the end product. The fluoride is converted to metallic scandium by heating with calcium in a tantalum crucible at elevated temperatures. A similar reduction is carried out with most rare earths. The metal is purified by distillation at 1,650 to 1,700°C under high vacuum in a tantalum crucible.

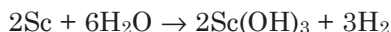
Scandium also may be produced by electrolysis of scandium chloride in a molten salt bath. The first preparation of the metal was carried out by this

electrolysis using an eutectic melt of lithium and potassium chlorides with scandium chloride at 700 to 800°C. Electrolysis methods usually yield impure metal containing mostly iron, silicon and other impurities.

Reactions

Scandium reacts with oxygen forming its only oxide, Sc_2O_3 . The reaction is slow on bulk metal at ordinary temperatures but rapid above 500°C.

The metal reacts with water liberating hydrogen. The reaction is slow at ambient temperatures:



Scandium metal reacts rapidly with most acids liberating hydrogen and forming salts upon evaporation of the solution. Scandium, however, is not attacked by 1:1 mixture of concentrated nitric acid and 48% hydrofluoric acid. A similar behavior is exhibited by yttrium and heavy rare earth metals.

Scandium forms all its compounds in 3+ oxidation state. This is the only valence known for the metal. These compounds include the oxide, Sc_2O_3 ; hydroxide, $\text{Sc}(\text{OH})_3$; chloride, ScCl_3 ; fluoride, ScF_3 ; sulfate, $\text{Sc}_2(\text{SO}_4)_3$, and the nitrate salt, $\text{Sc}(\text{NO}_3)_3$.

SELENIUM

[7782-49-2]

Symbol Se; atomic number 34; atomic weight 78.96; a Group VI A (Group 16) metallic element in the oxygen group of elements; electron configuration $[\text{Ar}]3\text{d}^{10}4\text{s}^24\text{p}^4$; valence states -2 , $+4$, $+6$; atomic radius $1.19\text{\AA}$; ionic radius, Se^{4+} $0.50\text{\AA}$ (for CN 6); Se^{6+} $0.42\text{\AA}$ (for CN 6); six naturally-occurring isotopes: Se-74 (0.89%), Se-76 (9.36%), Se-77 (7.64%), Se-78 (23.79%), Se-80 (49.61%), Se-82 (8.74%); nineteen radioactive isotopes in the mass range 65, 67–73, 75, 79, 81, 83–89, 91

History, Occurrence, and Uses

Selenium was discovered by Berzelius and Gahn in 1817 while investigating the lead chamber process for making sulfuric acid. They initially believed that the bottom of the lead chamber generating an offensive odor was due to presence of tellurium, a sulfur group element that was discovered thirty-five years earlier. Further studies indicated a new element, the chemical properties of which were very similar to tellurium. This new element was named selenium, derived from the Greek word *selene*, meaning moon. The name followed *tellus*, the Latin word for earth given to tellurium which chemically resembled the new element. Willoughby Smith in 1873 discovered photoresistivity in this metal; i.e., as the intensity of light exposure on the metal increased, its current resistance decreased.

Selenium is a very rare element. The metal does not occur in nature in free elemental form. Its abundance in the earth's crust is about 0.05 mg/kg. It

occurs in certain copper ores and sometimes with native sulfur. Some selenium containing minerals are eucairite, CuAgSe ; clausthalite, PbSe ; naumannite, Ag_2Se ; crookesite, $(\text{CuTlAg})_2\text{Se}$; and zorgite, PbCuSe .

Selenium has many industrial uses, particularly electronic and solid-state applications, which have increased phenomenally in recent years. This is attributed to its unique properties: (1) it converts light directly to electricity (photovoltaic action); (2) its electrical resistance decreases with increased illumination (photoconductivity); and (3) it is able to convert alternating current to direct current.

Selenium is used in photoelectric cells, solar cells, and as a rectifier in radio and television sets. It also was used historically in exposure meters in photography and as an ingredient of toning baths. It is used in photocopying documents. In the glass industry it is incorporated to pigments to color pink, orange, and ruby-red glass. Other applications are as a metallic base in preparing electrodes for arc light; as an additive to stainless steel; in chrome plating bath for inducing microcracks for corrosion control; in vulcanization of rubber; as a catalyst; and as a flame-proofing agent for electric switchboard cables.

Although a toxic metal, selenium in trace amounts is a nutritional element. Trace amounts added to cattle food are effective against muscular dystrophy in sheep and cattle.

Physical Properties

Selenium exists in several allotropic forms. Three distinct forms are (1) amorphous (2) crystalline and (3) metallic:

Amorphous forms exhibit two colors, occurring as a red powder of density 4.26 g/cm^3 that has a hexagonal crystal structure and a black vitreous solid of density 4.28 g/cm^3 . The red amorphous selenium converts to the black form on standing. Amorphous selenium melts at 60 to 80°C ; insoluble in water; reacts with water at 50°C when freshly precipitated; soluble in sulfuric acid, benzene and carbon disulfide.

Crystalline selenium exhibits two monoclinic forms: an alpha form constituting dark red transparent crystals, density 4.50 g/cm^3 . The alpha form converts to a metastable beta form of hexagonal crystal structure when heated to about 170°C . Both the crystalline forms are insoluble in water; soluble in sulfuric and nitric acids; very slightly soluble in carbon disulfide. Also, both the crystalline forms convert into gray metallic modification on heating.

The gray metallic form of selenium is its most stable modification. It constitutes lustrous gray to black hexagonal crystals; density 4.18 g/cm^3 at 20° ; melts at 217°C ; soluble in sulfuric acid and chloroform; very slightly soluble in carbon disulfide; insoluble in alcohol.

All forms of selenium vaporize at 684.8°C .

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$ (hexagonal, black)	0.0
$\Delta H_f^\circ(\text{cry})$ (monoclinic, black)	1.6 kcal/mol
ΔH_f° (amorphous, glassy)	1.2 kcal/mol

$\Delta H_f^\circ(\text{gas})$	54.3 kcal/mol
$\Delta G_f^\circ(\text{cry})$	0.0
$\Delta G_f^\circ(\text{gas})$	44.7 kcal/mol
$S^\circ(\text{cry})$ (hexagonal, black)	10.1 cal/deg mol
$S^\circ(\text{gas})$	42.2 cal/deg mol
$C_p(\text{cry})$ (hexagonal, black)	6.06 cal/deg mol
$C_p(\text{gas})$	4.98 cal/deg mol

Production

Selenium is recovered from anode muds or slimes in electrolytic refining of copper. Anode mud is treated with sulfuric acid and roasted. Selenium is converted to its dioxide, which vaporizes and is collected in a wet scrubber system.

Alternatively, raw anode slimes are aerated with hot dilute sulfuric acid to remove copper. Slimes are then mixed thoroughly with sodium carbonate and roasted in the presence of sufficient air. Sodium selenate formed is leached with water. Hydrochloric acid is added to this selenate solution. Treatment with sulfur dioxide precipitates elemental selenium. Alternatively, the selenate solution is evaporated to dryness. Sodium selenate is reduced to sodium selenide by heating with carbon at high temperatures. Sodium selenide is leached with water. Air is blown over the solution. Selenide is oxidized to elemental selenium which precipitates.

In another process known as soda-niter smelting, a slight variation of the above method, after removal of copper anode slimes are mixed with sodium carbonate and silica and charged to the furnace. First, slags are removed. To the molten mass, caustic soda and potassium nitrate are added. Selenium and tellurium separate into the slags. The slags are cooled, crushed, and leached with water. Sulfuric acid is added. This precipitates tellurium as dioxide. Sulfur dioxide is then passed through the solution precipitating elemental selenium.

Selenium obtained by the above methods is about 99% pure. High purity metal may be obtained by refining this commercial grade material. Commercial grade selenium is distilled to form highly purified metal. Another refining method involves melting the crude metal and bubbling hydrogen through it. Hydrogen selenide so formed is decomposed at 1,000°C. A third method involves oxidizing selenium to its dioxide and reducing the latter with ammonia at 600 to 800°C.

Selenium was recovered earlier from flue dusts from lead and copper sulfide ores. This process is now obsolete and no longer used.

Reactions

The chemical properties of selenium fall between sulfur and tellurium. Thus, selenium reacts with oxygen similarly to sulfur, forming two oxides, selenium dioxide, SeO_2 and trioxide, SeO_3 . The metal combines with halogens forming their halides. With nonmetals, selenium forms binary compounds exhibiting oxidation states +4 and +6.

Selenium reacts with electropositive metals and hydrogen forming

selenides, where its oxidation state is -2 . Thus, it combines with sodium to form sodium selenide, Na_2Se . When the metal is heated with hydrogen below 250°C , the product is hydrogen selenide, H_2Se .

The metal is not attacked by hydrochloric acid, nor does it react with dilute nitric and sulfuric acids. High purity selenium reacts slowly with concentrated nitric acid. The crude metal, however, dissolves in cold concentrated nitric acid.

When fused with caustic soda or caustic potash, sodium selenate, or potassium selenate, Na_2SeO_4 , or K_2SeO_4 is obtained.

Molten selenium combines with most metals forming selenides. Such metal selenides include Ag_2Se , Cu_2Se , HgSe , ZnSe , CdSe , PbSe , FeSe , FeSe_2 , and Sb_2Se_3 .

Selenium dissolves in sulfur and tellurium in all proportions.

Analysis

Selenium is converted to its volatile hydride by reaction with sodium borohydride, and the cold hydride vapor is introduced to flame AA for analysis. Alternatively, selenium is digested with nitric acid and 30% H_2O_2 , diluted and analyzed by furnace-AA spectrophotometer. The metal also may be analyzed by ICP-AES or ICP/MS. The wavelengths most suitable for its measurements are 196.0 nm for flame- or furnace-AA and 196.03 nm for ICP-AES. Selenium also may be measured by neutron activation analysis and x-ray fluorescence.

Selenite in aqueous solution can be measured by colorimetric or fluorometric methods. Selenite reacts with 2, 3-diaminonaphthalene to form a brightly colored fluorescent derivative that is extracted with hexane. The absorbance can be measured by a spectrophotometer at 480 nm, or the fluorescence may be measured by a fluorometer at 525 nm.

Toxicity

Although an essential nutrient metal at trace concentrations, selenium is highly toxic at moderate concentrations. Some of its compounds, such as hydrogen selenide, are very toxic. Exposure to Se metal fumes can cause severe irritation of eyes, nose and throat. The metal is listed by the US EPA as one of the priority pollutant metals in the environment.

SELENIUM DIOXIDE

[7446-08-4]

Formula SeO_2 ; MW 110.96

Synonyms: selenium oxide; selenious anhydride

Uses

Selenium dioxide is used to make other selenium compounds and as an oxidizing agent.

Physical Properties

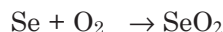
White tetragonal crystals; acidic taste; leaves a burning sensation; density 3.95 g/cm³; sublimes at 315°C forming greenish yellow vapors with a sour and pungent odor; melts at 340 to 350°C; vapor pressure 12.5 torr at 70°C; soluble in water, 38.4 g/100mL at 14°C; highly soluble in hot water 82.5 g/100mL at 65°C; soluble in benzene; moderately soluble in ethanol and acetone 6.7 and 4.4g/100mL solvent, respectively, at 15°C; sparingly soluble in acetic acid (1.11g/100mL at 14°C).

Thermochemical Properties

ΔH_f° (cry)	−53.86 kcal/mol
ΔH_f° (aq)	−52.97 kcal/mol

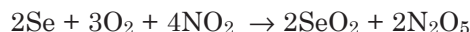
Preparation

Selenium dioxide is obtained by burning selenium metal in oxygen:



Selenium also forms a trioxide, SeO₃. In excess oxygen the product mixture may contain both dioxide and trioxide. The trioxide is unstable.

Selenium dioxide may be prepared by heating selenium with oxygen and nitrogen dioxide. Presence of excess oxygen would oxidize nitrogen dioxide to pentoxide, instead converting selenium dioxide to trioxide:



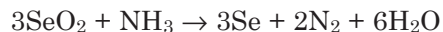
Selenium dioxide also may be produced by oxidation of selenium by nitric acid. The overall reaction may be written as follows:



Reactions

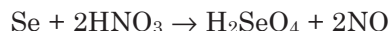
Selenium dioxide is reduced to selenium metal when heated with carbon and other reducing agents.

When heated with ammonia, selenium dioxide forms selenium, nitrogen and water:

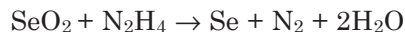


Ammonia reacts with selenium dissolved in ethanol to form ammonium ethyl selenite, NH₄(C₂H₅)SeO₃.

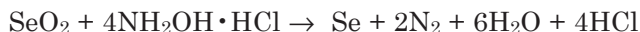
Reaction with nitric acid forms selenic acid:



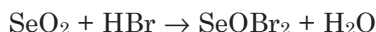
Selenium dioxide is reduced by hydrazine to black amorphous selenium:



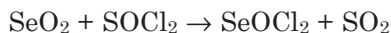
Hydroxylamine hydrochloride reduces selenium dioxide to reddish-brown amorphous selenium:



The dioxide rapidly absorbs hydrogen halides, forming selenium oxyhalides:



Reaction with thionyl chloride yields selenium oxychloride:



Analysis

Elemental composition: Se 71.16% O 28.84%. Aqueous solution may be analyzed for selenium metal by flame or furnace-AA or ICP-AES. A benzene or acetone solution may be analyzed directly by GC/MS. The characteristic mass ions for its identification should be 112, 110, 108, 80, and 78.

Toxicity

The compound is toxic by ingestion. Symptoms of the poisoning effects of selenium dioxide are similar to those of selenium metal. Selenium dioxide vapors are highly irritating to eyes, nose and respiratory tract.

SELENIUM HEXAFLUORIDE

[7783-79-1]

Formula SeF_6 ; MW 192.95

Uses

The hexafluoride is a gaseous insulator in electrical works.

Physical Properties

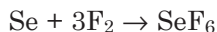
Colorless gas; refractive index 1.895; density 3.25 g/L at -28°C ; liquefies at -34.5°C ; freezes at -50.8°C ; sublimes at -63.8°C ; insoluble in water

Thermochemical Properties

ΔH_f°	-267.0 kcal/mol
ΔG_f°	-243.0 kcal/mol
S°	75.0 cal/deg mol
C_p	26.4 cal/deg mol

Preparation

Selenium hexafluoride is prepared by passing fluorine gas over finely divided selenium in a copper vessel:



Analysis

Elemental composition: Se 40.92%, F 59.08%. The gas may be dissolved in nitric acid and dilute hydrofluoric acid and the solution appropriately diluted and analyzed for selenium (see Selenium). The hexafluoride may be decomposed with ammonia at 200°C and product selenium analyzed by AA, and gaseous products nitrogen and hydrogen fluoride diluted with helium and analyzed by GC-TCD or GC/MS. Alternatively, selenium hexafluoride diluted with helium is introduced onto the GC injector port and analyzed by GC/MS. Molecular ions have masses 194, 192, 196, and 190.

SELENIUM OXYCHLORIDE

[7791-23-3]

Formula SeOCl_2 ; MW 165.85

Synonym: selenyl chloride

Uses

Selenium oxychloride is a solvent for synthetic phenolic resins and many other substances.

Physical Properties

Pale yellow or colorless liquid; corrosive; refractive index 1.651 at 20°C; density 2.42 g/mL at 22°C; freezes at 8.5°C; boils at 176.4°C; decomposes at 176.4°C; decomposes in water forming hydrochloric acid and selenious acid; soluble in carbon disulfide, carbon tetrachloride, chloroform, benzene, and toluene.

Preparation

Selenium oxychloride may be prepared by several methods: (1) by passing chlorine gas into a suspension of selenium dioxide in carbon tetrachloride, (2) by heating thionyl chloride, SOCl_2 , with selenium dioxide, (3) by dehydration of dichloroselenious acid, $\text{H}_2\text{Se}(\text{Cl}_2)\text{O}_2$, and (4) by fusion of selenium dioxide, selenium, and calcium chloride.

Analysis

Elemental composition: Se 47.60%, Cl 42.75%, O 9.65%. The compound is decomposed by water and the solution analyzed for selenium (see Selenium). The oxychloride may be mixed with a suitable organic solvent such as toluene or methylene chloride, diluted appropriately with the solvent, and analyzed by GC/MS. The characteristic mass ions (molecular ions) for identification are 166, 164, 170, and 168. Other mass ions are 80, 78, 150, and 148.

Toxicity

The oxychloride is a strong irritant to skin. Eye contact can damage vision.

The compound is highly toxic by ingestion and inhalation.

SILICON

[7440-21-3]

Symbol Si; atomic number 14; atomic weight 28.086; a Group IV (Group 14) carbon family element; electron configuration $[\text{Ne}]3s^23p^2$; valence +4; atomic radius 1.173Å; electronegativity 1.8; three naturally-occurring stable isotopes: Si-28(92.23%), Si-29(4.67%), Si-30 (3.10%); twelve artificial radioactive isotopes in the mass range 24–27, 31–38; longest-lived radioisotope Si-32, a beta-emitter with a half-life 160 years.

History, Occurrence, and Uses

Gay Lussac and Thenard in 1809 obtained very impure amorphous silicon by passing silicon tetrafluoride over heated potassium. Berzelius in 1823 prepared elemental silicon in high purity by the same method. He also obtained silicon by heating potassium fluosilicate with potassium metal. Deville produced crystalline silicon in 1854 by electrolysis of a molten mixture of impure sodium aluminum chloride containing 10% silicon and a small quantity of aluminum.

Silicon is the second most abundant element on earth after oxygen. It occurs in nature combined with oxygen in various forms of silica and silicates. Silicates have complex structures consisting of SiO_4 tetrahedral structural units incorporated to a number of metals. About 90% of the earth's crust is made up of silica and naturally-occurring silicates. Silicon is never found in nature in free elemental form. Among all elements silicon forms the third largest number of compounds after hydrogen and carbon. There are well over 1,000 natural silicates including clay, mica, feldspar, granite, asbestos, and hornblende. Such natural silicates have structural units containing orthosilicates, SiO_4^{4-} , pyrosilicates $\text{Si}_2\text{O}_7^{6-}$ and other complex structural units, such as, $(\text{SiO}_3)_n^{2n-}$ that have hexagonal rings arranged in chains or pyroxenes $(\text{SiO}_3^{2-})_n$ and amphiboles, $(\text{Si}_4\text{O}_{11}^{6-})_n$ in infinite chains. Such natural silicates include common minerals such as tremolite, $\text{Ca}_2\text{Mg}_5(\text{OH})_2\text{Si}_8\text{O}_{22}$; diopside, $\text{CaMg}(\text{SiO}_3)_2$; kaolin, $\text{H}_8\text{Al}_4\text{Si}_4\text{O}_{18}$; montmorillonite, $\text{H}_2\text{Al}_2\text{Si}_4\text{O}_{12}$; talc, $\text{Mg}_3[(\text{OH})_2\text{SiO}_{10}]$; muscovite (a colorless form of mica), $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$; hemimorphite, $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$; beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; zircon, ZrSiO_4 ; benitoite, $\text{BaTiSi}_3\text{O}_9$; feldspars, KAlSi_3O_8 ; zeolites, $\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$; nephrite, $\text{Ca}(\text{Mg},\text{Fe})_3(\text{SiO}_3)_4$; enstatite, $(\text{MgSiO}_3)_n$; serpentine, $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$; jadeite, $\text{NaAl}(\text{SiO}_3)_2$; topaz, $\text{Al}_2\text{SiO}_4\text{F}_2$; and tourmaline, $(\text{H},\text{Li},\text{K},\text{Na})_9\text{Al}_3(\text{BOH})_2\text{Si}_4\text{O}_{19}$. Many precious gemstones are silicate based. Such gems include beryl, emerald, aquamarine, morganite, topaz, tourmaline, zircon, amazon stone and moonstone.

Silica, the other most important class of silicon compounds, exists as sand, quartz, flint, amethyst, agate, opal, jasper, and rock crystal. It is discussed separately under Silicon Dioxide. Silicates and silica have many applications

in numerous fields. They are used in making cements and concretes for building materials, glasses and glasswares, ceramics, pigments, adsorbents, paper boards, fillers, detergents, precious gems, catalysts, and water-softeners. Ferrosilicon, an important alloy of iron and silicon, is used as an alloying agent in the manufacture of steel and as a reducing agent in the preparation of magnesium, chromium and other metals. Silicones, or the organosilicon oxide polymers consisting of the structural unit $-R_2Si-O-$ are used as lubricants; and in making rubbers, plastics, electrical coatings, adhesives, paints and varnishes; and as water repellents for textiles, papers and concrete.

Elemental silicon has some of the most important applications in this electronic age. One of the major applications is in computer chips. The single crystals of crystalline silicon are used for solid-state or semiconductor devices.

Silicon of hyperpurity, doped with trace elements, such as boron, phosphorus, arsenic, and gallium is one of the best semiconductors. They are used in transistors, power rectifiers, diodes and solar cells. Silicon rectifiers are most efficient in converting a-c to d-c electricity. Hydrogenated amorphous silicon converts solar energy into electricity.

Physical Properties

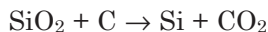
Exists in two allotropic modifications. Crystalline silicon is made up of grayish-black lustrous needle-like crystals or octahedral platelets; cubic structure; Amorphous silicon is a brown powder. Other physical properties are: density 2.33g/cm^3 at 25°C ; melts at $1,414^\circ\text{C}$; high purity liquid silicon has density 2.533 g/cm^3 at its melting point; vaporizes at $3,265^\circ\text{C}$; vapor pressure 0.76 torr at $2,067^\circ\text{C}$; Mohs hardness 6.5. Brinell hardness 250; poor conductor of electricity; dielectric constant 13; critical temperature 4°C ; calculated critical pressure 530 atm ; magnetic susceptibility (containing $0.085\%\text{Fe}$) 0.13×10^{-6} ; insoluble in water; dissolves in hydrofluoric acid or a mixture of hydrofluoric and nitric acids; soluble in molten alkalis.

Thermochemical Properties

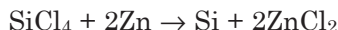
$\Delta H_f^\circ(\text{cry})$	0.0
$\Delta H_f^\circ(\text{amor})$	1.0 kcal/mol
$\Delta H_f^\circ(\text{gas})$	108.9 kcal/mol
$\Delta G_f^\circ(\text{cry})$	0.0
$\Delta G_f^\circ(\text{gas})$	98.3 kcal/mol
$S^\circ(\text{cry})$	4.50 cal/deg mol
$S^\circ(\text{gas})$	40.12 cal/deg mol
$C_p(\text{cry})$	4.78 cal/deg mol
$C_p(\text{gas})$	5.32 cal/deg mol
ΔH_{fus}	12.08 kcal/mol
Thermal conductivity(at 25°C)	0.835 W/cmK
Coefficient of linear expansion (at 25°C)	$3.0 \times 10^{-6}/^\circ\text{C}$

Production

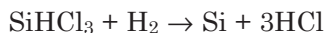
Elemental silicon is produced commercially by heating silica with carbon (coke) in an electric furnace using carbon electrodes:



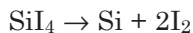
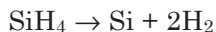
The product obtained is about 96 to 98% purity. Repeated leaching forms about 99.7% purified product. Alternatively, lower grade silicon is converted to its halide or halosilane, which is then reduced with a high purity reducing agent. Hyperpure silicon for semiconductor applications can be made by several methods. Such processes include reduction of silicon tetrachloride with highly pure zinc:



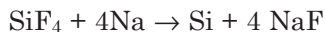
or by reducing trichlorosilane with hydrogen at 1,150°C using a silicon filament on which deposition of silicon occurs:



or by heating silane or silicon tetraiodide to elevated temperatures:



or by reducing silicon tetrafluoride with sodium:



Several processes are known to achieve growth of single crystals of silicon for semiconductors. One such method developed in 1918 is known as Czocharski process or Teal-Little method. The process involves dipping a single crystal “seed” into molten silicon held at the melting point. The seed is properly oriented by rotation and the molten silicon is allowed to freeze gradually over it and the seed is slowly withdrawn. The growth rate is controlled by melt temperature and heat losses from the crystal. Growth rates are usually in the range of 2.5 cm/hour but can vary with diameter. Crystals of varying sizes have been produced by this method. The common sizes of crystals usually range between 75 to 125 mm in diameter and about 100 cm long. Pure quartz crucibles or silicon pedestals are employed to carry out single crystal’s growth.

Reactions

Elemental silicon is relatively stable in most substances at ordinary temperatures. Silicon shows similarity with other elements of its group, especially with germanium in many chemical properties. It forms tetravalent compounds with tetrahedral geometry almost exclusively. However, only in silicon monoxide, SiO, is its valence +2. Also, unlike carbon, silicon does not form unsaturated double or triple bond compounds. Silicon dissolves in germanium

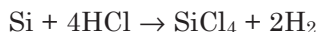
in all proportions but is not miscible with tin or lead. When heated with carbon at elevated temperatures in an electric furnace, silicon carbide, SiC, or carborundum is obtained. The carbide, however, is made in commercial scale from silica. The Si-Si bond having bond energy 42.5 kcal/mol is weaker than the C-C bond, which has a bond energy 58.6 kcal/mol. The latter is comparable to Si-C bond (57.6 kcal/mol). Similarly Si-H bond (energy 75.1 kcal/mol) is weaker than the C-H bond (87.3 kcal/mol). On the other hand Si-O bond (89.3 kcal/mol) is stronger than the C-O bond (70.0 kcal/mol).

Silicon forms two oxides, silica or the dioxide, SiO₂, and a divalent monoxide, SiO. The latter is obtained by heating silica with elementary silicon at 1,450°C in vacuum. Silicon sublimes as its monoxide, which on rapid cooling forms light brown amorphous SiO:



At ordinary temperatures, the metal surface is coated with a very fine thin amorphous film of its dioxide, about 2 to 3 nm thick. Silicon combines with oxygen forming innumerable silicates. A few silicates have been mentioned above.

Silicon combines with halogens at elevated temperatures forming silicon tetrahalides. With chlorine, reaction occurs at 450°C forming silicon tetrachloride, SiCl₄. The tetrahalides also are obtained when silicon is heated with anhydrous hydrogen chloride, bromide and iodide:



With hydrogen fluoride, the products are fluosilicic acid, H₂SiF₆, and hydrogen:



When heated with nitrogen at a temperature above 1,300°C, silicon nitride is produced:



With hydrogen, a series of silanes having a general formula Si_nH_{2n+2} are obtained. Silicon forms binary silicides with several metals when heated at very high temperatures.

Silicon reacts with strong bases forming silicates and liberating hydrogen. Silicon is attacked by hydrofluoric acid if there is no oxide layer over it. However, since the metal has a very thin oxide film over its surface, a mixture of nitric and hydrofluoric acid is effective in dissolution of the metal. While nitric acid dissolves the oxide layer, the metal is then attacked by hydrofluoric acid.

Analysis

Silicon can be identified from its line spectra. Trace quantities of the metal

can be measured accurately by flame-AA using nitrous oxide-acetylene flame. Silica, silicates, or other silicon compounds may be digested with concentrated nitric acid, diluted and analyzed. ICP-AES, ICP/MS and neutron activation method also may be applied.

Toxicity

Inhalation of silica dusts or silicate mineral dusts can cause silicosis and other lung diseases.

SILICON CARBIDE

[409-21-2]

Formula SiC; MW 40.097

Synonym: carborundum

Uses

Silicon carbide is widely used as an abrasive in grinding and cutting glasses; in polishing glass and sharpening stones. It is used in the manufacture of porcelain, refractory brick, furnace linings, and emery paper. The compound also is used in semiconductor technology.

Physical Properties

Greenish blue to black crystalline solid; hexagonal or cubic crystals; diamond-like structure; density 3.217g/cm³; exceedingly hard, Mohs hardness 9.5; sublimates at about 2,700°C; dielectric constant 7.0; electron mobility >100 cm²/volt-sec; hole mobility >20cm²/volt-sec; band gap energy 2.8 eV; insoluble in water and acids; solubilized by fusion with caustic potash.

Preparation

Silicon carbide is prepared by heating fine silica with carbon (coke) and a little salt and sawdust in an electric furnace.

Analysis

Elemental composition: Si 70.03%, C 29.97%. The carbide can be characterized by its physical properties and by x-ray crystallography. Silicon content may be determined by flame-AA after solubilizing the carbide by fusion with potassium hydroxide and extracting water-soluble potassium silicate with water.

SILICON DIOXIDE

[7631-86-9]

Formula SiO₂; MW 60.085

Synonym: silica

Occurrence and Classifications

Silicon dioxide occurs almost everywhere on earth. It is one of the most important and abundant oxides on earth, constituting about 60% weight of the earth's crust as silica itself or in combination with other metal oxides in silicates. It commonly is found as sand in the vast ocean and river shores, their beds, deserts, rocks, and minerals.

Silicon dioxide exists in several structural forms: polymorphic crystalline silica, synthetic quartz crystals, amorphous silica, and vitreous silica. This classification is not complete as there are other forms of silica synthesized for specialized applications. Various forms of silica are mentioned briefly below.

Crystalline Silica: Three principal polymorphic forms exist at atmospheric pressure. These are quartz, tridymite, and cristobalite. Quartz is stable below 870°C. It transforms to tridymite form at about 870°C. Tridymite is stable up to 1,470°C and transforms to cristobalite at 1,470°C. High cristobalite melts around 1,723°C. Other than these three polymorphs, there are also three high pressure phases of crystalline silica: keatite, coesite, and stishovite.

Quartz occurs in granite, sand, crystals, and sandstone. Quartz also has several crystalline varieties such as purple amethyst, colorless rock crystal, and yellow citrine. Flint, agate, and chert, etc. are other forms of quartz. Quartz is an excellent insulator. It does not break under temperature changes because of its low coefficient of expansion. Fused quartz transmits ultraviolet light.

Quartz exhibits two slightly varying atomic arrangements. One is the beta- or high quartz that consist of linked tetrahedral-forming helixes in which the hexagonal unit cell contains three SiO_2 units and in which Si—O bond distance is 1.62Å. The density of high quartz at 600°C is 2.53 g/cm³. The other form, known as the low, or alpha quartz, has a density of 2.65 g/cm³ at 0°C. Here the Si—O bond distance differs slightly, measured as 1.597 and 1.617Å. Low quartz is the most common form of silica. It exhibits piezoelectric properties for which it has a high commercial value. Thermal inversion of quartz occurs around 573°C in which one form converts to the other form by slight displacement of atoms in their structural arrangements. The presence of impurities can affect the inversion temperature. Quartz also is optically active; individual crystals are either levorotatory or dextrorotatory.

Tridymite is another form of crystalline silica stable between 870 and 1,470°C at atmospheric pressure. It is found in volcanic rocks and has been identified in many stony meteorites. Tridymite also exists in various forms. It has six different modifications that undergo thermal inversions from one to another. Its density at 200°C is about 2.22 g/cm³. The hexagonal unit cell contains four SiO_2 units. The Si—O bond distance is 1.52Å.

Cristobalite is the third crystalline silica form stable at high temperature. It exists between 1,470 to 1,723°C. A metastable form may exist below 1,470°C. Cristobalite has three-layer sequences of SiO_4 . The oxygen atoms of the tetrahedral SiO_4 have cubic close-packed structure. Cristobalite is found in some volcanic rocks.

Three high pressure crystalline silica have been made in polymorph phas-

es. One of them, keatite has a tetragonal structure with twelve SiO_2 units in the unit cell. Keatite has been prepared by crystallization of amorphous precipitated silica from dilute sodium or potassium hydroxide solutions at 380 to 585°C and 345 to 1,180 atm pressure in a hydrothermal bomb. It transforms to cristobalite when heated at 1,620°C for a few hours. Coesite is the second most dense phase of silica. Its density is 3.01 g/cm³. Coesite is prepared by heating a mixture of sodium metasilicate and diammonium hydrogen phosphate at 500 to 800°C at 15,000 to 35,000 atm. It also can be made by oxidizing silicon with silver carbonate under pressure.

Stishovite is the most dense phase of silica. Its density is 4.35 g/cm³. It has a rutile-type crystal structure in which the silicon atom is octahedrally surrounded by six oxygen atoms. Four Si—O bonds are 1.76Å and two 1.81Å. Stishovite has been prepared similarly to coesite but at temperatures between 1,200 to 1,400°C and a pressure above 150,000 atm. Both the coesite and stishovite are found in nature in certain meteorite craters resulting from meteorite impacts.

In addition to the above crystalline phases silica also exists in a few microcrystalline forms. Such micro crystalline or cryptocrystalline silicas occur in nature and include diatomaceous earth, flint, and chert. They are mostly of biogenic origin forming from compaction of amorphous silica over geologic time.

Amorphous Silica: The term amorphous silica refers to aggregate of small particles with high specific surface area. They lack crystal structure and do not form a sharp x-ray diffraction pattern. They are known in several forms such as colloidal silica, precipitated silica, silica gels, and fumed silica. The surface of such amorphous silica may contain silanol (SiOH) groups or can be anhydrous.

Amorphous silica in nature may originate from aquatic organisms, secreted as amorphous solid in the form of shells, plates, or skeletons. Amorphous silica also is found in volcanic ash or in precipitated material from the hot supersaturated waters of hot springs.

Amorphous silica can be hydrated up to about 14% or made anhydrous. They usually contain siloxane ($-\text{Si}-\text{C}-\text{Si}-$) or silanol ($-\text{Si}-\text{O}-\text{H}$) bonds. At the surface there may be silane ($-\text{Si}-\text{H}$) or organic silicon ($-\text{Si}-\text{O}-\text{R}$ or $-\text{Si}-\text{C}-\text{R}$) bonds. Hydrated amorphous silica is made by polymerization of silicic acid in water in slightly acidic solution at a low temperature. At ambient temperature, such hydrated silica is stable and does not lose water below 60°C. Amorphous silica is broadly categorized into vitreous silica or glass, silica M and microamorphous silica. Vitreous silica is made by fusing quartz. Silica M is prepared by irradiating amorphous or crystalline silica with high-speed neutrons. It is a dense form of amorphous silica and is thermally unstable. When heated at 930°C for several hours, silica M converts to quartz.

Microamorphous silica is made of particles with diameters less than 1µm. They have very high surface areas, usually greater than 3m²/g. These microamorphous silica are an aggregation of colloidal ultimate particles that broadly include sols, gels, powder, and porous glass. An important class of

microamorphous silica constitutes what is known as microparticulate silica. These are the silicas precipitated from aqueous solution such as sol and gel or that are formed at high temperatures by condensation from vapor phase, such as pyrogenic silica.

Pyrogenic silica is made by vaporizing sand at 2,000°C and then cooling the vapors, or oxidizing silicon tetrachloride vapors at high temperatures. It has a SiO_2 content above 99.7% and density of 2.16 g/cm³. The ultimate particle size is in the range 1 to 100 nm. When heated at 105°C, the weight loss is between 0.5 to 2.5%. There is no additional loss in the weight when the material is further heated at 1,200°C.

Silica sol is a stable dispersion of fine particles, while gel has a three-dimensional continuous structure. SiO_2 content in sol range between 10–50%, while that in dry silica gels is between 96.5 to 99.6%. Density of dry gels is 2.22 g/cm³ and sols 2.20 to 2.30 g/cm³. Weight loss in sols at 105°C is between 50–80%.

Silica gel is a rigid, continuous three-dimensional network of spherical colloidal particles. If the pores are filled with water it is known as hydrogel. The surface of silica gel consists of silanol (Si—O—H) groups or siloxane (Si—O—Si) groups. It also may have an organic surface. Silica gels are precipitated from water. When dried below 150°C, silanol surfaces are developed. When heated at 300 to 1,000°C, the silanol surfaces dehydrate to form siloxane surface. Silica gels are made by many ways. One method involves mixing sodium silicate with a strong mineral acid. This forms a silica hydrosol. It is set to a rigid mass, which is broken up mechanically to form hydrogel particles. Hydrogel is washed and then dried. The final gel properties, such as, density, hardness, surface area, and pore volume depend on silica concentration, temperature, pH, gelling time, and rate of drying. Hydrolysis of silicon tetrachloride, ethyl silicate and other silicon compounds also produces gels. These gels are dense, having very small pore size, and are of high purity.

Vitreous Silica: Vitreous silica is a glass form of silica composed of SiO_2 . It may be transparent, translucent, or opaque. It has a number of abnormal and anomalous properties in thermal expansion, viscosity, bulk density, compressibility, and elasticity. These properties depend on thermal history and preparation method. Vitreous silica exhibits high resistance to chemical attack. At ambient temperature, it is not attacked by any chemical except hydrofluoric acid.

Transparent vitreous silica is made by electric melting of natural quartz minerals such as sand in vacuum. It also may be made by fusing quartz in flame or by vapor phase hydrolysis or oxidation of pure silicon compounds by heating electrically or using a flame or plasma. Translucent form is made by fusion of high purity quartz sand crystals.

Uses

The largest amount of silica is used in building materials. It is the main constituent of ceramics, such as refractory silica bricks. It also is the basic raw material of all types of glasses. Vitreous silica is used to make laboratory

glassware, mirrors, prisms, cells, windows, and other optical devices. Synthetic quartz, because of its piezoelectric properties, is used in electrical oscillators, filters, transducers, and many consumer products, such as electronic watches.

Amorphous silica is used as a pigment and filler in paints and coatings. It also is used as an abrasive, absorbent and catalyst support. Silica gel is a common desiccant and adsorbent. It is used in analytical chemistry as a packing material in chromatography columns and in clean-up of organic extracts to remove interference in trace analysis of organic pollutants.

Precipitated silica is used to produce molecular sieves, as an anti-caking agent, and as filler for paper and rubber. Hydrophobic silica is a defoaming agent.

SILICON HYDRIDES

Silicon forms a series of hydrides known as silanes, formula $\text{Si}_n\text{H}_{2n+2}$, where n is the number of silicon atoms in the molecule. This general formula for the silicon hydrides is similar to the $\text{C}_n\text{H}_{2n+2}$ for the alkane class of hydrocarbons. The names, synonyms, CAS Registry numbers, formulas, and molecular weights of the first four hydrides are given below:

Name	Synonyms	CAS No.	Formula	MW
silane	silicane, monosilane, silicon tetrahydride	[7803-62-5]	SiH_4	32.12
disilane	disilicane	[1590-87-0]	Si_2H_6	62.22
trisilane	trisilicane, trisilanepropane	[7783-26-8]	Si_3H_8	92.32
tetrasilane	tetrasilicane, tetrasilane butane	[7783-29-1]	Si_4H_{10}	122.42

Uses

Silane is used to produce hyperpure silicon for semiconductors. Also, it is used to prepare other silicon compounds. Higher silanes do not have any practical applications.

Physical Properties

Silane: Colorless gas; repulsive odor; density 1.44 g/L; liquefies at -111.8°C ; freezes at -185°C ; decomposes slowly in water; insoluble in alcohol, ether, chloroform and silicon tetrachloride; soluble in caustic potash solution.

Disilane: Colorless gas; density 2.865 g/L; liquefies at -14.5°C ; liquid density 0.686 g/mL at -20°C ; freezes at -132.5°C ; slowly decomposes in water;

soluble in alcohol, benzene, and carbon disulfide.

Trisilane: Colorless liquid; density 0.743 g/mL at 0°C; freezes at -117.4°C; boils at 52.9°C; vapor density 4.15 g/L at atmospheric pressure; decomposes in water; decomposes in carbon tetrachloride.

Tetrasilane: Colorless liquid; density 0.79 g/mL at 0°C; freezes at -108°C; boils at 84.3°C; vapor density 5.48 g/L at STP; decomposes in water.

Thermochemical Properties

<i>Silane</i> :	ΔH_f°	8.2 kcal/mol
	ΔG_f°	13.6 kcal/mol
	S°	48.9 cal/deg mol
	C_p	10.2 cal/deg mol
<i>Disilane</i>	ΔH_f°	19.2 kcal/mol
	ΔG_f°	30.4 kcal/mol
	S°	65.1 cal/deg mol
	C_p	19.3 cal/deg mol
<i>Trisilane</i>	ΔH_f° (liq)	22.1 kcal/mol
	ΔH_f° (gas)	28.9 kcal/mol

Preparation

Silicon hydrides can be prepared by several methods. A few methods are outlined below. Silane and its higher homologs can be made by treating magnesium silicide, Mg_2Si with 20% hydrochloric acid in an atmosphere of hydrogen. An equation for monosilane is given below:



The product mixture may contain higher silanes at over 50% yield, depending on reaction conditions.

Another preparative method involves treating magnesium silicide with ammonium bromide in liquid ammonia in a current of hydrogen. The process forms 70 to 80% yield of mono- and disilanes. The reaction is shown below:



Zinc, lithium, and aluminum silicides also may be used instead of magnesium silicide in the above preparations.

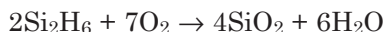
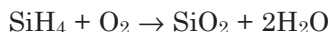
Silane also may be prepared by the reaction of silicon tetrachloride with lithium aluminum hydride in ether:



Two other methods for preparing silane are treating silica gel with aluminum oxide in presence of hydrogen and by electrolysis of an aqueous solution of sodium or ammonium chloride using a silicon-aluminum alloy as the positive electrode.

Reactions

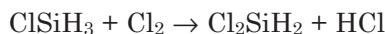
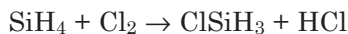
Silanes are flammable substances. Silane ignites in air spontaneously. Liquid disilane explodes in contact with air:



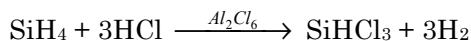
Silanes do not react with water under normal conditions. In the presence of alkalis base hydrolysis readily occurs. Thus, reactions with caustic potash solution yield potassium silicate with evolution of hydrogen:



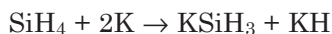
Silane reacts explosively with halogens at ordinary temperatures forming halogenated silane derivatives. Reaction is vigorous to moderate at very low temperatures:



Silane forms halo derivatives with hydrogen halides. The reaction occurs moderately at ordinary temperature catalyzed by aluminum halides:



Silane reacts with alkali metals dissolved in a solvent such as 1,2-dimethoxyethane to form the metal derivative MSiH_3 and hydrogen or metal hydride:



Reaction with methanol in the presence of copper catalyst yields tetramethoxysilane, $\text{Si}(\text{OCH}_3)_4$, trimethoxysilane, $\text{SiH}(\text{OCH}_3)_3$, and dimethoxysilane, $\text{SiH}_2(\text{OCH}_3)_2$

Analysis

Silanes are hydrolyzed in basic solution (e.g., KOH solution) (see Reactions). The silicate solution is analyzed for silicon by flame-AA. Hydrogen evolved from such base hydrolysis of silanes is measured quantitatively to

determine the number of silicon atoms and hydrogen atoms in silane. Thus, one molecule of mono-, di-, tri-, and tetrasilanes liberate 4, 7, 10, and 13 molecules of H_2 respectively (i.e., for each Si—Si and Si—H bond present in the silane, one molecule of H_2 is liberated).

Hazard

Silanes are pyrophoric substances igniting and exploding spontaneously in air. They also liberate toxic hydrogen chloride gas. The gaseous monosilane and the vapors of higher silanes are irritants to the respiratory tract. Chronic exposure to low concentration can cause pulmonary edema.

SILICON TETRACHLORIDE

[10026-04-7]

Formula $SiCl_4$; MW 169.90; bond energy 91.06 kcal/mol

Synonym: tetrachlorosilane

Uses

Silicon tetrachloride was first prepared by Berzelius in 1823. It is used widely in preparing pure silicon and many organosilicon compounds such as silicone. It also is used to produce smoke screens in warfare.

Physical Properties

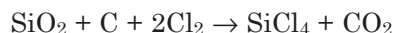
Colorless fuming liquid; suffocating odor; density 1.52 g/mL; freezes at $-68.9^\circ C$; boils at $57.7^\circ C$; vapor pressure 235 torr at $25^\circ C$; critical temperature $235^\circ C$; critical pressure 35.45 atm; critical volume $326\text{ cm}^3/\text{mol}$; decomposes in water forming silicic acid and HCl; soluble in benzene, toluence, chloroform, and ether.

Thermochemical Properties

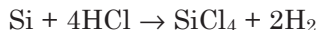
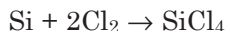
ΔH_f° (liq)	-164.2 kcal/mol
ΔH_f° (gas)	-157.0 kcal/mol
ΔG_f° (liq)	-148.1 kcal/mol
ΔG_f° (gas)	-147.5 kcal/mol
S° (liq)	57.3 cal/deg mol
S° (gas)	79.0 cal/deg mol
C_p (liq)	34.7 cal/deg mol
C_p (gas)	21.6 cal/deg mol
ΔH_{fus}	1.82 kcal/mol
ΔH_{vap}	6.86 kcal/mol

Preparation

Silicon tetrachloride is prepared by heating silicon dioxide and carbon in a stream of chlorine:

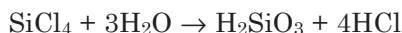


Also, the compound may be prepared by heating silicon with chlorine or dry hydrogen chloride:

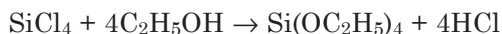


Reactions

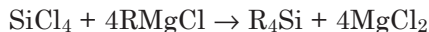
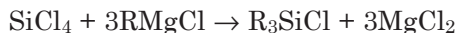
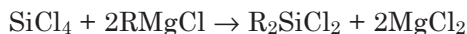
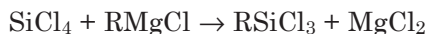
Silicon tetrachloride decomposes in water forming silicic acid (precipitated silica) and hydrochloric acid:



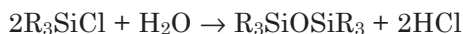
Reactions with alcohols yield esters of orthosilicic acid. For example, with ethanol the product is tetraethyl orthosilicate or tetraethoxysilane, $\text{Si}(\text{OC}_2\text{H}_5)_4$:



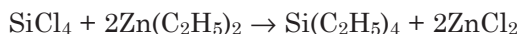
An important class of organosilicon compounds known as silicones that are used as lubricants, resins, elastomers, and antifoaming agents in high-vacuum diffusion pumps are synthesized from silicon tetrachloride. Silicon tetrachloride reacts with Grignard reagents, RMgCl to form monoalkyltrichlorosilanes, RSiCl_3 , dialkyldichlorosilanes, R_2SiCl_2 , trialkylmonochlorosilanes, R_3SiCl , and tetraalkylsilanes, R_4Si :



The alkylchlorosilanes on hydrolysis form various types of silicones. For example, hydrolysis of trialkylmonochlorosilanes yields silyl ethers, $\text{R}_3\text{SiOSiR}_3$, which form silicones:



Silicon tetrachloride reacts with diethylzinc to form tetraethylsilane. This compound was synthesized by Friedel and Crafts in 1863, the first organosilicon compound:



Silicon tetrachloride reacts with alkyl chloride and sodium to form the

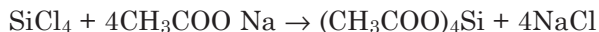
same tetraalkylsilane:



Silicon tetrachloride reacts with acetic anhydride to form silicon tetraacetate (tetraacetoxyasilane). This reaction was discovered by Friedel and Ladenburg in 1867:



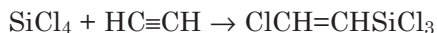
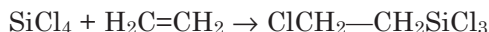
Silicon tetraacetate can also be made by the reaction of silicon tetrachloride with sodium acetate. In general any carboxylate salt of silicon can be prepared from silicon tetrachloride by this reaction:



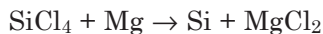
Ladenburg in 1873 synthesized phenyltrichlorosilane, $\text{C}_6\text{H}_5\text{SiCl}_3$ by heating silicon tetrachloride with diphenylmercury:



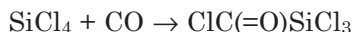
Silicon tetrachloride undergoes addition with olefinic and acetylenic unsaturated hydrocarbons. In these addition reactions, one chlorine atom adds to one carbon atom of the double or triple bond while the rest of the unit $-\text{SiCl}_3$ attaches to the other carbon atom forming a silicon—carbon bond:



Silicon tetrachloride is reduced to metallic silicon when heated with sodium, potassium, and a number of metals:



It reacts with carbon monoxide to form a compound with a silicon carbon bond:



Reaction with excess amine forms amine derivatives of silicon:



Analysis

Elemental composition: Si 16.52%, Cl 83.48%. The compound may be added slowly to water and decomposed. The aqueous solution may be analyzed for silicon (see Silicon). An aliquot of the solution may be measured for chloride

ion by titration with a standard solution of silver nitrate or by ion chromatography. Also, the concentration of HCl in the solution may be determined by titration against a standard solution of NaOH. Silicon tetrachloride may be dissolved in a suitable organic solvent and the solution analyzed by GC/MS.

Toxicity

The vapors are very toxic and irritating to the eyes, throat, and mucous membrane.

SILICON TETRAFLUORIDE

[7783-61-1]

Formula SiF_4 ; MW 104.08

Synonym: tetrafluorosilane

Uses

Unlike silicon tetrachloride, the tetrafluoride has minor applications. The compound is used in preparation of other silicon compounds. It also is an intermediate in gravimetric analysis of silica.

Physical Properties

Colorless gas; very pungent odor; fumes heavily in moist air; density of the gas 4.69 g/L; heavier than air, density in air 3.5 (air = 1); sublimates at -95.7°C ; solidifies at -90.2°C (under pressure); critical pressure 50atm; decomposes in water forming silicic acid and hydrofluoric acid.

Thermochemical Properties

ΔH_f° -386.0 kcal/mol

ΔG_f° -375.9 kcal/mol

S° 67.5 cal/deg mol

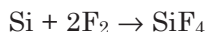
C_p 17.6 cal/deg mol

Preparation

Silicon tetrafluoride is prepared by heating silica with dilute hydrofluoric acid at high temperatures:



Also, the tetrafluoride may be obtained by heating the elements:



Reactions

See Silicon Tetrachloride Reactions

Analysis

Elemental composition: Si 26.97%, F 73.03%. The gas is bubbled slowly through water to decompose into silicic acid and hydrofluoric acid. HF is analyzed for fluoride ion by fluoride-selective electrode or by ion chromatography. Silicon in the aqueous solution can be measured by AA or ICP.

Toxicity

Silicon tetrafluoride is a toxic gas. Inhalation can cause severe irritation of the respiratory tract.

SILVER

[7440-22-4]

Symbol Ag; atomic number 47; atomic weight 107.87; a Group 1B (Group 11) coinage metal positioned between copper and gold; electron configuration $[\text{Kr}]4d^{10}5s^1$ valence +1, +2; most common valence +1; atomic radius 1.442Å; ionic radius of Ag in crystals with coordination numbers 4 and 6 1.00Å and 1.15Å, respectively; ionization potential ($\text{Ag} \rightarrow \text{Ag}^+$) 7.576 eV; standard electrode potential E° for $\text{Ag}^+ + e^- \leftrightarrow \text{Ag}$ 0.800 V; two naturally-occurring stable isotopes: Ag-107 (51.84%) and Ag-109 (48.16%); twenty-nine radioactive isotopes in the mass range 94–106, 108, 110–124.

History, Occurrence, and Uses

Silver is one of the oldest metals, known since ancient times. It is a precious metal worldwide, used in ornaments, coins, and utensils. The symbol Ag for this element is derived from the Latin word, *argentum*. Silver occurs in nature in native form, commonly associated with gold. It is found in most lead and copper ores. The principal mineral of silver is argentite, Ag_2S [1332-04-3]. Some other silver minerals include pyrargyrite, Ag_3SbS_3 [15123-77-0]; proustite, Ag_3AsS_3 [15152-58-4]; polybasite, $\text{Ag}_{16}\text{Sb}_2\text{S}_{11}$ [53810-31-4]; cerargyrite, AgCl [14358-96-4]; stephanite, Ag_5SbS_4 [1302-12-1]; and tetrahedrite, $\text{Cu}_3(\text{AsSb})\text{S}_3$. Abundance of silver in the earth's crust is estimated to be 0.075 mg/kg and its average concentration in sea water is 0.014 µg/L.

Silver and its alloys and compounds have numerous applications. As a precious metal, silver is used in jewelry. Also, one of its alloys, sterling silver, containing 92.5 weight % silver and 7.5 weight % copper, is a jewelry item and is used in tableware and decorative pieces. The metal and its copper alloys are used in coins. Silver-copper brazing alloys and solders have many applications. They are used in automotive radiators, heat exchangers, electrical contacts, steam tubes, coins, and musical instruments.

Some other uses of silver metal include its applications as electrodes, catalysts, mirrors, and dental amalgam. Silver is used as a catalyst in oxidation-reductions involving conversions of alcohol to aldehydes, ethylene to ethylene oxide, and ethylene glycol to glyoxal.

Many silver compounds, such as silver nitrate, silver chloride, and silver oxides, have wide commercial applications. The most important uses are in photography and batteries (see individual compounds).

Physical Properties

White metal with brilliant metallic luster; face-centered cubic crystals; density 10.43 g/cm³ at 20°C, and 9.18 g/cm³ at 1,100°C; melts at 961.8°C; vaporizes at 2,162°C; vapor pressure 5 torr at 1,500° C; pure metal has the highest electrical and thermal conductive of all metals, electrical resistivity of pure metal at 25°C 1.617×10⁻⁶ ohm-cm; elastic modulus 71GPa (10.3×10⁶ psi); Poisson's ratio 0.39 (hard drawn), 0.37 (annealed); viscosity of liquid silver 3.97 centipoise at 1,043°C; thermal neutron absorption cross section 63±1 barns; insoluble in water; inert to most acids; attacked by dilute HNO₃ and concentrated H₂SO₄; soluble in fused caustic soda or caustic potash in the presence of air.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	68.1 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	58.8 kcal/mol
S° (cry)	10.2 cal/deg mol
S° (gas)	41.3 cal/deg mol
C_p (cry)	6.07 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	2.70 kcal/mol
ΔH_{vap}	68.0 kcal/mol
Thermal conductivity	4.29 W/cmK
Coefficient of linear expansion (at 25°C)	18.9×10 ⁻⁶ /°C

Production

Many processes are known for recovery of silver from its ores. These depend mostly on the nature of the mineral, its silver content, and recovery of other metals present in the ore. A few processes are briefly outlined below.

Silver is usually extracted from high-grade ores by three common processes that have been known for many years. These are amalgamation, leaching, and cyanidation. In one amalgamation process, ore is crushed and mixed with sodium chloride, copper sulfate, sulfuric acid, and mercury, and roasted in cast iron pots. The amalgam is separated and washed. Silver is separated from its amalgam by distillation of mercury.

In the cyanidation process the ore is crushed and roasted with sodium chloride and then treated with a solution of sodium cyanide. Silver forms a stable silver cyanide complex, $[\text{Ag}(\text{CN})_2]^-$. Adding metallic zinc to this complex solution precipitates silver.

Several leaching processes are known. One such process, known as the Patera process, developed in the mid 19th century, involves roasting ore with sodium chloride followed by leaching with sodium thiosulfate solution. Silver

is precipitated as silver sulfide, Ag_2S , by adding sodium sulfide to the leachate. In the Clandot process, leaching is done with ferric chloride solution. Addition of zinc iodide precipitates silver iodide, AgI . AgI is reduced with zinc to obtain silver.

The above processes are applied for extraction of silver from high-grade ores. However, with depletion of these ores, many processes were developed subsequently to extract silver from low-grade ores, especially lead, copper, and zinc ores that contain very small quantities of silver.

Low grade ores are concentrated by floatation. The concentrates are fed into smelters (copper, lead, and zinc smelters). The concentrates are subjected to various treatments before and after smelting including sintering, calcination, and leaching. Copper concentrates are calcined for removal of sulfur and smelted in a reverberatory furnace to convert into blister copper containing 99 wt% Cu. The blister copper is fire-refined and cast into anodes. The anodes are electrolytically refined in the presence of cathodes containing 99.9% copper. Insoluble anode sludges from electrolytic refining contain silver, gold, and platinum metals. Silver is recovered from the mud by treatment with sulfuric acid. Base metals dissolve in sulfuric acid leaving silver mixed with any gold present in the mud. Silver is separated from gold by electrolysis.

Lead and zinc concentrates can be treated in more or less the same manner as copper concentrates. Sintering lead concentrates removes sulfur and following that smelting with coke and flux in a blast furnace forms impure lead bullion. The lead bullion is drossed with air and sulfur and softened with molten bullion in the presence of air to remove most impurities other than silver and gold. Copper is recovered from the dross and zinc converts to its oxide and is recovered from blast furnace slag. The softened lead obtained above also contains some silver. The silver is recovered by the Parkes Process. The Parkes process involves adding zinc to molten lead to dissolve silver at temperatures above the melting point of zinc. On cooling, zinc-silver alloy solidifies, separating from the lead and rising to the top. The alloy is lifted off and zinc is separated from silver by distillation leaving behind metallic silver.

The unsoftened lead obtained after the softening operation contains silver in small but significant quantities. Such unsoftened lead is cast into anode and subjected to electrolytic refining. The anode mud that is formed adhering to these anodes is removed by scraping. It contains bismuth, silver, gold, and other impurity metals. Silver is obtained from this anode mud by methods similar to the extraction of anode mud from the copper refining process discussed earlier.

If the low-grade ore is a zinc mineral, then zinc concentrate obtained from the flotation process is calcined and leached with water to remove zinc. Silver and lead are left in leach residues. Residues are treated like lead concentrates and fed into lead smelters. Silver is recovered from this lead concentrate by various processes described above.

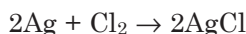
Reactions

At ordinary temperatures, silver is not affected by dry or moist air. At a

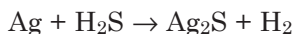
temperature just above its melting point, silver absorbs a large volume of oxygen, which is greater than ten times its own volume. Such oxygen absorption, however, drops dramatically below its melting point and, just before solidification, absorbed oxygen is ejected violently. Solid silver also dissolves oxygen but to a much lesser extent, the volume absorbed depending on temperature.

Silver also absorbs hydrogen above 800°C. Exposure of pure silver at about 810°C alternatively to both hydrogen and oxygen gases embrittles the metal.

Silver reacts with halogens at elevated temperatures forming halides. With chlorine, the reaction occurs above 455°C, the melting point of silver chloride, to form molten silver chloride:



Silver reacts readily with hydrogen sulfide at ambient temperature forming silver sulfide:



Most metal sulfides react with silver at room temperature, tarnishing the surface with a sulfide coating.

Silver is attacked by nitric acid at all concentrations. The reaction is exothermic producing silver nitrate with liberation of nitric oxide and nitrogen dioxide:



Silver dissolves very slowly in hot concentrated sulfuric acid forming silver sulfate, Ag_2SO_4 . Reaction with hydrochloric acid is slow and stops after initial formation of a protective layer of silver chloride on the surface.

Aqueous solutions of alkali metal cyanides attack silver in the presence of oxygen forming a double salt:



This reaction is used for extraction of silver from its ores.

Silver is tarnished by sulfur, sulfur dioxide, and mercury. It also is attacked by ozone, hydrogen peroxide, chromic acid, ferric sulfate, and permanganate solutions.

Analysis

Silver metal and its contents in silver alloys and salts can be measured at trace levels by various instrumental techniques such as flame- and furnace-AA, ICP-AES, ICP/MS and x-ray fluorescence methods. It is solubilized by digestion with nitric acid prior to analysis. The AA measurement may be carried out at the wavelength 328.1 nm and ICP analysis at 328.07 nm. ICP/MS is the most sensitive technique while x-ray fluorescence is relatively less sen-

sitive. Silver also can be measured by neutron activation analysis.

Toxicity

All water-soluble silver salts are toxic and ingestion can cause severe poisoning (see Silver Nitrate). Silver is listed by the US EPA as one of the priority pollutant metals in the environment.

SILVER ACETYLIDE

[7659-31-6]

Formula Ag_2C_2 ; MW 239.76; Structure $\text{AgC}\equiv\text{CAg}$

Synonym: silver(I) acetylide

Uses

Silver acetylide is used in explosives. It is a powerful detonator.

Physical Properties

White powder; unstable; explodes when subjected to heat or shock.

Preparation

Silver acetylide is prepared by passing acetylene through a silver salt solution.

Hazard

The compound presents severe explosion hazard when shock or heat is applied.

SILVER BROMIDE

[7785-23-1]

Formula AgBr ; MW 187.77

Uses

Silver bromide is used in photographic film and plates. It also is used in photochromic glass. In medicine it is used as a topical anti-infective and astringent agent.

It occurs as the mineral bromyrite.

Physical Properties

Yellow cubic crystals or powder; refractive index 2.253; darkens on exposure to light; Mohs hardness 2.5; density 6.47g/cm^3 ; melts at 432°C ; vaporizes at $1,502^\circ\text{C}$; insoluble in water, alcohol, and most acids; slightly soluble in dilute ammonia and ammonium carbonate solutions; sparingly soluble in concentrated ammonia solution (0.33 g/100mL 10% ammonia solution at 12°C);

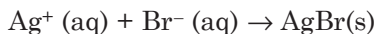
soluble in alkali cyanide solutions.

Thermochemical Properties

ΔH_f°	-24.0 kcal/mol
ΔG_f°	-23.2 kcal/mol
S°	25.6 cal/deg mol
C_p	12.5 cal/deg mol
ΔH_{fus}	2.18 kcal/mol
ΔH_{vap}	47.3 kcal/mol

Preparation

Silver bromide is prepared by double decomposition reaction. An aqueous solution of alkali bromide, such as sodium or potassium bromide, is slowly added to an aqueous solution of silver nitrate:



The precipitate is washed repeatedly with hot water. Preparation should be in a dark room under a ruby red light.

Analysis

Elemental composition: Ag 57.45%, Br 42.55%. Silver bromide is digested with aqua regia, diluted and analyzed for silver by flame- or furnace-AA, or ICP-AES. The aqueous solution is appropriately diluted and analyzed for bromide by ion chromatography.

SILVER CHLORIDE

[7783-90-6]

Formula AgCl; MW 143.32

Uses

Silver chloride is used in silver plating and to obtain pure silver. The salt also finds applications in photography and optics; in photochromic glass; and in electrodes and batteries. It is used to make antiseptic silver solution. It occurs as the mineral cerargyrite.

Physical Properties

White granular powder or cubic crystals; refractive index 2.071; darkens on exposure to light; density 5.56 g/cm³; Moh's hardness 2.5; melts at 455°C; vaporizes at 1,547°C; vapor pressure 1 and 5 torr at 912 and 1,019°C; insoluble in water, alcohol and dilute acids; soluble in ammonia solution and concentrated sulfuric acid, alkali cyanide, ammonium carbonate; also soluble in potassium bromide and sodium thiosulfate solutions.

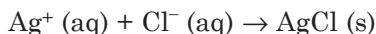
Thermochemical Properties

ΔH_f°	-30.4 kcal/mol
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ΔG_f°	-26.2 kcal/mol
S°	23.0 cal/deg mol
C_p	12.1 cal/deg mol
ΔH_{fus}	3.15 kcal/mol
ΔH_{vap}	47.6 kcal/mol

Preparation

Silver chloride is prepared by slowly adding an alkali metal chloride solution to a hot solution of silver nitrate. The solution mixture is boiled:



The precipitate is washed with hot water. The product is purified by dissolving in ammonia solution, filtering out any insoluble residues, and then adding hydrochloric acid to reprecipitate silver chloride. Preparation should be carried out in the dark in ruby red light.

Analysis

Elemental composition: Ag 75.26%, Cl 24.74%. The salt is dissolved in concentrated sulfuric acid, diluted, and analyzed for silver (see Silver). Solid powder may be characterized by its physical properties and its reaction with cyanide ion, forming the complex ion $[\text{Ag}(\text{CN})_2]^-$.

SILVER CHROMATE

[7784-01-2]

Formula Ag_2CrO_4 ; MW 331.73

Uses

Silver chromate is a catalyst in conversion of alcohol to aldol. It's formation signals the end point in argentometric titration in measuring halides.

Physical Properties

Red monoclinic crystals or brownish-red powder; density 5.625 g/cm³; insoluble in water; soluble in nitric acid, ammonia and solutions of alkali cyanides and chromates.

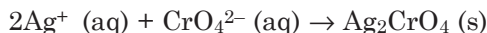
Thermochemical Properties

ΔH_f°	-174.9 kcal/mol
ΔG_f°	-153.4 kcal/mol
S°	52.0 cal/deg mol
C_p	34.0 cal/deg mol

Preparation

Silver chromate is prepared by slowly adding a solution of potassium chro-

mate to a solution of silver nitrate:



The precipitate is washed with hot water.

Analysis

Elemental composition: Ag 65.03%, Cr 15.68%, O 19.29%. The salt is dissolved in nitric acid, diluted, and analyzed for silver and chromium by flame- and furnace-AA, ICP-AES or other instrumental method to measure the contents of these metals.

SILVER CYANIDE

[506-64-9]

Formula AgCN; MW 133.89

Uses

Silver cyanide is used for silver plating.

Physical Properties

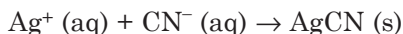
Grayish-white hexagonal crystals; density 3.95 g/cm³; decomposes at 320°C; insoluble in water, alcohol or dilute acids; moderately soluble in concentrated ammonia; soluble in concentrated boiling nitric acid; also soluble in alkali cyanide solutions.

Thermochemical Properties

ΔH_f°	34.9 kcal/mol
ΔG_f°	37.5 kcal/mol
S°	25.6 cal/deg mol
C_p	15.9 cal/deg mol

Preparation

Silver cyanide is prepared by adding a solution of an alkali cyanide to a solution of silver nitrate:



Analysis

Elemental composition: Ag 80.57%, C 8.97%, N 10.46%. The salt is digested with concentrated nitric acid, diluted, and analyzed for silver.

Toxicity

Silver cyanide is highly toxic by ingestion. Contact with skin and eyes can cause severe irritation.

LD₅₀ oral (rat): 123mg/kg